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DEPARTMENT BULLETIN No. 1452

Washington, D. C. ▼ November, 1926

PROPERTIES OF THE COLLOIDAL SOIL MATERIAL

By

M. S. ANDERSON and SANTE MATTSON, Associate Chemists
Soil Chemical Division, Bureau of Soils

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By M. S. Anderson and Sante Mattson, *Associate Chemists, Soil Chemical Division, Bureau of Soils*

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INTRODUCTION

Although properties of the soil have been extensively investigated from the viewpoint of colloidal behavior, comparatively little information is available on the properties of the colloidal material itself. Early ideas concerning the properties of soil colloids have been based largely on interpretation of properties of the whole soil. Recently, however, with improvement in methods for isolating the colloidal material from the larger soil particles, quantitative determinations have been made of certain properties of the separated colloidal material.

The adsorptive capacity, chemical composition and binding power of various soil colloidal materials have already been studied in this bureau (*20*, *47*, *40*).[1] This bulletin presents data on a number of other properties of the colloidal material. The object of this investigation was to throw light on the nature of the colloidal soil material through a study of properties that characterize it as a colloid, rather than to explain any particular field property of the soil; therefore some properties were studied that do not have any obvious relation to the field behavior of soils.

[1] Numbers in parentheses in italic refer to "Literature cited," p. 44.

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THE SOIL COLLOIDS STUDIED

In the course of various investigations in this bureau, colloidal materials have been isolated from some 50 soils and subsoils from different parts of the United States, and certain characteristics of these materials have been determined. It was therefore possible to select for this study eight colloids which represent fairly well the major variations shown in one or two properties by a considerable number of different colloids. The ultimate chemical compositions [2] of the eight colloidal materials isolated especially for this study are shown in Table 1.

TABLE 1.—*Chemical composition of colloidal soil materials studied*

Name of colloid	SiO_2	TiO_2	Fe_2O_3	Al_2O_3	MnO	CaO	MgO	K_2O
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Fallon	50.49	.51	10.77	16.73	0.121	2.36	5.32	2.24
Sharkey	50.13	.46	8.70	21.70	.035	1.48	2.54	1.86
Marshall	44.94	.47	8.91	22.15	.126	1.12	1.95	2.07
Susquehanna	43.92	1.08	5.70	33.82	.006	.18	.39	.92
Sassafras	40.93	.70	11.98	29.55	.033	.37	1.37	1.04
Huntington	36.65	.45	11.07	29.98	.192	.53	.72	1.93
Norfolk	38.46	.93	11.43	33.38	.005	.28	.46	.55
Aragon	15.86	3.54	22.67	34.38	.068	.21	29	.27

Name of colloid	Na_2O	P_2O_5	SO_3	Ignition loss	Total	Organic matter	H_2O at 110° C.	Mols. SiO_2 / Mols. $Al_2O_3+Fe_2O_3$
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	
Fallon	0.54	0.37	0.11	10.05	99.61	1.79	12.15	3.62
Sharkey	.24	.69	----	12.56	100.40	3.83	11.46	3.11
Marshall	.19	.70	.21	16.86	99.70	7.94	8.96	2.73
Susquehanna	.29	.21	.09	13.50	100.11	1.86	2.38	1.99
Sassafras	.31	.11	.02	14.44	100.85	1.88	5.07	1.85
Huntington	.33	.98	.27	16.82	99.92	5.74	4.61	1.68
Norfolk	.31	.28	.05	13.16	99.30	2.18	3.51	1.60
Aragon	.33	.26	----	21.59	99.47	5.96	4.51	.55

The colloids are named for the soils from which they were extracted. The locations and depths of the soil samples are as follows:

Fallon loam. Depth 0 to 12 inches. Six miles west of Fallon, Churchill County, Nev.

Sharkey clay. Depth 0 to 4 inches. Near Valley Park, Issaquena County, Miss.

Marshall silt loam. Depth 0 to 14 inches. Two miles west of Mynard, Case County, Nebr.

Sassafras silt loam. Depth 8 to 22 inches. Near Easton, Talbot County, Md.

Huntington loam. Depth 0 to 8 inches. One mile west of Seneca, Montgomery County, Md.

Norfolk fine sandy loam. Depth 12 to 36 inches. One-fourth mile south of Scottsville, Wayne County, N. C.

Susquehanna clay. Depth about 4 feet. Takoma Park, Montgomery County, Md.

Aragon soil. Depth 13½ to 17 feet. Turrialba, Costa Rica.

[2] Analyses were made by the fusion method for soils, essentially as described in the "Methods of Analysis" of the Association of Official Agricultural Chemists (5). The organic matter was determined by dry combustion, multiplying the CO_2 evolved by the factor 0.471.

Description of the Sharkey, Marshall, Huntington, Sassafras, Susqehanna, Norfolk, and Fallon[3] soil types are given in a previous publication of this bureau (*35*). The sample of Aragon soil was selected because of its unusual chemical composition.

The colloids were isolated essentially as described in a previous publication (*20*, *p. 16*). The soils were treated with large quantities of water and the turbid extracts passed through a supercentrifuge to grade out noncolloidal particles. In the preparation of these samples no ammonia was used, except in the case of the Aragon soil, which without ammonia, settled clear very quickly in pure water. Dispersion was facilitated by rubbing the plastic mass of the fine soil material under water. The products obtained were, in each case, submicroscopic and were comparable to the preparations previously studied.

PROPERTIES OF COLLOIDAL SOIL MATERIALS

SIZE OF PARTICLES

Size of particles has generally been considered a fundamental distinguishing characteristic of materials in a colloidal condition. In fact, in many instances differences in colloidal properties have been assumed to be proportional to particle size. It should be borne in mind, however, that such a proportionality between particle size and properties holds only when one deals with a particular kind of colloidal material For example, the properties of different preparations of colloidal sulphur parallel to a certain extent the size of the particles (*41*), but it is not to be expected that a sulphur sol and a gold sol having particles of the same size would have the same properties. The chemical composition of colloidal materials extracted from different soils has been shown to vary widely. It is thus probable that differences in behavior of the various colloidal soil materials may be in part dependent upon chemical composition, and not entirely a function of size of particles.

The colloidal material exists in the soil chiefly as a gel; that is, as an intimate aggregation of ultimate particles. When the material is dispersed in water the dilute sols are stable, but the suspended matter may consist of both ultimate particles and aggregates. Determinations of size by most methods would not distinguish between ultimate particles and aggregates; nevertheless such determinations should characterize the different colloids more or less, even if the particles are chiefly aggregates, provided the materials are dispersed by a uniform treatment. If the different materials are dispersed in the same manner, variation should occur in the size of aggregates owing to variation in the nature of the materials.

The upper limit of size of particles in the different soil colloids was of course determined by the method of preparation, the maximum diameter of the particles being about 0.3 micron. It is evident, however, that the upper limit of size offers no indication of average size, inasmuch as the samples used contained all the colloid passing

[3] The sample of Fallon soil used contained about 0.5 per cent soluble salts. It was selected for this work particularly on account of its highly impervious character. The soluble salts were, of course, removed by the procedure followed in isolating colloidal material.

through the supercentrifuge.[4] These preparations probably differed somewhat from those of Bradfield, who must have discarded a part of the finest particles, since he recovered that portion of the colloid which was thrown out when greater centrifugal force was utilized (*9*).

Ultra filters did not seem well adapted to the determination of the size of particles in the colloidal soil material, inasmuch as the material clogs the pores very quickly and renders the filter entirely impervious to colloidal particles. Among the methods proposed for determining particle size, that of Siedentopf and Zsigmondy (*50*) seemed most practical for determining differences in the average size of particles. This method consists in counting with an ultramicroscope the number of particles in a known volume containing a known weight of material of determined specific gravity, and then calculating size by assuming a definite form of particles. In the present study the particles were assumed to be spherical and to have the specific gravities shown in Table 2. The accuracy of this method depends to a great extent upon the character of the material examined. The error involved is primarily one of imperfect visibility which arises from two causes: (1) Some particles may be so small as to be invisible, and (2) the index of refraction of certain particles may be so near that of water as to render them practically invisible.[5]

The colloidal materials from seven soils were examined by the method of Siedentopf and Zsigmondy. The suspensions directly from the centrifuge were diluted with optically pure water in such proportions that in the final dilution an average of one to three particles were visible in the field at one time. The blank count of the water averaged 0.035 of a particle. In order to promote dispersion and to prevent as far as possible the aggregation of primary particles, ammonia was added in each case to N/200. The particles were observed with an ultramicroscope of the Siedentopf-Zsigmondy type, which was provided by the microchemical division, Bureau of Chemistry.

The average diameters of the particles in seven colloidal soil materials are shown in Table 2. The surface of smooth spherical particles of this size and the number of such particles that would be present in 1 gram of material are also given in Table 2.

TABLE 2.—*Average size of colloidal soil particles*

Kind of colloid	Average diameter of colloidal particles	Surface per gram of colloid particles	Number of particles per gram of colloid divided by 10^{12}
	Millimicrons	*Square meters*	
Susquehanna	141	15.7	263
Norfolk	129	17.1	322
Sassafras	128	17.0	335
Huntington	111	20.4	505
Marshall	106	21.5	613
Sharkey	91	24.2	960
Fallon	102	21.3	680

[4] Pasteur-Chamberland filters were used for concentrating the colloidal suspensions. The solutions passing through them were always clear and contained only 8 to 15 parts per million of dissolved material.

[5] Attempts were made to increase the visibility of particles by the addition of small quantities of methylene blue and other dyes. No significant advantage was obtained, however, by such treatment.

The accuracy of the determination of particle size was undoubtedly much greater in the case of the Susquehanna, Norfolk, and Sassafras colloids than in the case of the Fallon. In the former, most of the particles gave distinct, brilliant spots of light, whereas the latter contained many particles near the extreme limit of visibility. It is probable that in the case of the Fallon colloid a comparatively large number of particles were actually invisible either because of extremely small size or low index of refraction. Such an error in counting would ascribe to the Fallon colloid a particle size larger than was actually present. It is therefore probable that the particles of the Fallon colloid were actually the smallest of the group studied.

Since the turbidity of a suspension is more or less proportional to the size of the particles or aggregates, some evidence concerning comparative particle size in colloid suspensions was obtained by observing the comparative turbidities. Suspensions containing 0.1 gram per liter of each of the seven colloidal materials were made up and arranged in the order of relative turbidity. The Susquehanna colloid showed greatest turbidity, the Norfolk less, and so on in the same order as the particle size determined by the count method, with the exception of the Fallon, which was least turbid. This evidence serves further to substantiate the conclusion stated above that the particles of the Fallon colloid were in reality the smallest of the group studied.[6]

The size of particles shown in Table 2 is in general accord with the results obtained by Ehrenberg and Given (*11*). They found an average diameter of 140 millimicrons for a colloidal clay sample prepared by long subsidence of an ammoniacal suspension. The results obtained by Svedberg and Nichols (*51*) on a colloidal clay show also a similar magnitude. They used a centrifugal method for measuring the minimum size and the ultramicroscopic count method for measuring average size of particles. The smallest particles were 80 millimicrons in diameter and the average only slightly larger.

Ultramicroscopic determinations doubtless give a fairly accurate estimate of particle size in sols of colloidal soil material, provided all the assumptions involved in the determination are true; namely, that all the particles are primary ones, and all visible, and that the specific gravity of the particles as determined in water represents the true volume relation to mass. It has just been shown that, in some cases at least, there is strong probability that some of the material is invisible. There is no direct evidence indicating whether the particles counted are all primary ones, all aggregates, or a mixture of both. The latter case seems most probable. Furthermore, since the specific gravity of the material was determined on the basis of its weight when dried at 110° C., it is probable that in the swollen and perhaps hydrated state of the colloid in the suspension, particle size may have been considerably different from that calculated when dry weight was used.

SPECIFIC GRAVITY

Specific gravity is considered a definite constant of most liquids and solids. But in the case of materials which appear to be sub-

[6] The case with which water is removed from the different colloidal suspensions is probably also indicative of comparative particle size. The Fallon, Sharkey, and Marshall colloids very quickly clog Pasteur-Chamberland filters, thus making the filtration process very slow. On the other hand, the Susquehanna and Norfolk colloids filter very rapidly.

microscopically porous, widely different results may be obtained when different liquids are used for the determination.[7] Certain investigators regard this variation in apparent specific gravity as being chiefly due to unequal penetration of different liquids into the minute capillaries or micropores. If this is the true explanation, penetration is evidently not governed solely by viscosity of the liquid nor by the size of its molecules, since penetration does not always parallel either viscosity or molecular weight. According to one theory, penetration would be governed chiefly by surface tensions; that is, by whether or not the liquid tends to displace a solid-air or liquid-air interface and thus wet the surface of the capillaries. In the absence of a definitely established explanation, penetration might be vaguely ascribed to an " affinity " of the solid for the liquid.

A very different explanation for the fact that microscopically porous substances show varying specific gravities in different liquids is offered by Harkins and Ewing (*23*). They hold that liquids of low viscosity completely fill the micropores, but are so greatly compressed therein by an adhesional force that the liquid densities are markedly increased. Differences in apparent specific gravity are thus due to different liquids showing variable increases in density on being compressed. It is suggested that, in the micropores of an activated charcoal, an adhesional force equivalent to approximately 20,000 atmospheres compresses water about 25 per cent and ether 40 per cent.

It is obviously important to know whether the specific gravity of the soil colloidal material varies in different liquids. A constant specific gravity in different liquids would indicate a " true " specific gravity. Such a constant should serve to distinguish the different soil colloids, since they vary considerably in their chief constituents, silica, alumina, iron, and organic matter. Different specific gravities in different liquids would at least indicate that the soil colloids possess a property in common with activated charcoals and other substances presumably submicroscopically porous in structure.

Washburn and Bunting (*53*) have determined the porosity of certain clays and ceramic products in gases, in water, and in vaseline. Porosities indicated by determinations in water and vaseline were practically identical; air, helium, and hydrogen in many cases indicated greater pore volumes than were shown by the liquids. No data are available in the literature on the specific gravities of isolated soil colloids.

In connection with the present investigation, determinations were made of the specific gravities of six colloidal soil materials in both water and toluene. The air-dried colloidal material, ground to pass a 50-mesh sieve, was dried at 110° C. for 48 hours. It was then transferred while hot to a pycnometer[8] and allowed to cool in a desiccator. After weighing, the pycnometer was half filled with liquid (either water or toluene) and was placed in an evacuated chamber, where the liquid was allowed to boil for several minutes to remove air. The pycnometer was then placed on a steam bath over night to remove air and to promote penetration of the liquid. After

[7] Harkins and Ewing (*23*) give the apparent specific gravity of an activated charcoal as 0.8 in mercury, 2.1 in water, and 2.4 in ether.

[8] A specific gravity bottle of Gay Lussac type was used. It was found advisable to equip it with a glass cap fitting over the stopper to reduce evaporation.

cooling, liquid was added to the point of overflow. A piece of cover glass was placed over the opening in the stopper to reduce evaporation and the pycnometer was placed in a desiccator containing some of the same liquid as used in the determination. The desiccator was kept in a constant temperature bath a little above room temperature for four hours. When constant temperature was attained, the cover glass was taken off and any liquid that had overflowed through the stopper was removed. A weighing was then quickly made.[9] Duplicate determinations of specific gravity made in this way usually checked within 0.003.

Table 3 shows the specific gravities of six colloids in water and in toluene, determined by the procedure described above:

TABLE 3.—*Specific gravities of soil colloids in water and toluene*

Kind of colloid	Specific gravity in water	Specific gravity in toluene	Difference
Fallon	2.766	2.616	0.150
Sassafras	2.748	2.642	.106
Sharkey	2.718	2.582	.136
Susquehanna	2.715	2.554	.161
Norfolk	2.708	2.639	.069
Marshall	2.627	2.412	.215

The specific gravity of each colloid is higher in water than in toluene, and in each case the difference in the specific gravities is considerably greater than the experimental error. Obviously, neither the specific gravity in water nor that in toluene can be accepted as being necessarily the true specific gravity of the material, although possibly both series of values may be near the truth.

If the apparent specific gravities in the table approximate the true values, the colloidal materials would have specific gravities about the same as those of the commoner soil minerals, quartz being 2.65, the feldspars 2.55 to 2.75, and the micas 2.7 to 3.1. Also, if the apparent specific gravities parallel the true values, it would appear that the different colloids do not differ greatly. Variations in the apparent specific gravities of the different colloids show no relation to variations in chemical compositions of the materials, unless possibly the low specific gravity of the Marshall colloid may have been due to its relatively high content of organic matter. This apparent absence of relationship between specific gravity and chemical composition may possibly be due to the number of constituents present, which vary somewhat independently, or to a fault in the procedure of the determination.[10]

The fact that each of the colloids has a lower specific gravity in toluene than in water indicates that, in this respect at least, the soil colloidal material is to be classed with finely porous materials. The pores, however, need not necessarily be rigid, as in charcoal,

[9] The temperature in the desiccator being higher than room temperature, there was no danger of overflow through the capillary while the pycnometer was being weighed.

[10] Although the same procedure was followed closely in the determination of the specific gravity of each colloid, there is no assurance that drying at 110° C. constituted exactly comparable conditions in each case. In the subsequent treatments with liquid there may have been varying quantities of air not eliminated.

nor part of a regular structure; they may be irregular interstices formed by the irregular agglomeration of submicroscopic particles. The magnitude of the difference in specific gravity in the two liquids varies considerably with the different soil colloids. In the case of most colloids, the difference is about as great as Harkins and Ewing (*23*) found for the difference between the specific gravities of activated charcoals in water and benzene.

If the compressibility hypothesis is used to explain the different specific gravities of the soil colloids in water and toluene, it would be necessary to assume that water is held by the colloids with a far greater adhesional force than toluene, since the specific gravity of the material is higher in water than in toluene and yet toluene is more compressible than water. The compressibility explanation would, therefore, involve a further explanation of differences in adhesional forces, or "affinities."

The results might also be explained on the grounds of unequal penetration of the two liquids, water, which gives the higher specific gravity, penetrating more completely than toluene. It should be noted in this connection that, although some precautions were taken in the specific gravity determinations to promote the penetration of the liquid and draw out adsorbed or occluded air, it was impossible to evacuate the colloid under high temperature without altering the nature of the material. This explanation also reduces itself to the somewhat vague concept of varying affinities of the material for water and for toluene, since it would be necessary to explain why water replaces adsorbed air better than toluene.

HEAT OF WETTING

It has been shown that the heats of wetting of colloidal materials from different soils vary widely (*2*, *8*); hence the heat of wetting determination serves to characterize the colloidal material and to a certain extent distinguishes one kind from another.

The quantity of heat evolved by the colloid on wetting is indicative of the nature of the material. However, specific conclusions regarding the ultimate structure or constitution of the colloids can not be drawn from measurements of the heats of wetting, since the nature of the reactions involved when a substance is wetted is not well understood. The heat evolved by a substance on being wetted is of course a manifestation of the net energy change accompanying adsorption of a liquid. Two different hypotheses have been suggested to explain what takes place in the process of adsorption and to account for this energy change.

The older hypothesis, which is supported by recent work of Lamb and Coolidge (*31*) and of Harkins and Ewing (*23*) on activated charcoals, holds that the adsorbed liquid is compressed at the surface of the adsorbent with a force equivalent to 20,000 to 37,000 atmospheres in the case of certain charcoals. The compressive force is considered as being due to an attraction between the molecules of the adsorbent and the molecules of the liquid, whereas the heat evolved is largely the heat of compression of the adsorbed liquid.

Patrick and his coworkers (*44*) have advanced a different hypothesis to account for the heat of wetting of silica gel. They regard the heat of wetting as arising from the formation of new interfaces having a smaller total surface energy. Silica gel is conceived of as an

agglomeration of silica particles each surrounded by a film of water. Capillary spaces a few millimicrons in diameter are formed by the agglomeration of particles. The water-air interface of these capillaries is enormous when the material is nearly dry. When the material is immersed in water the capillaries are filled with adsorbed water and the water-air interface disappears; hence the evolution of heat. When the material is immersed in benzene, the adsorption of benzene in the capillaries replaces the water-air interface with a water-benzene interface.

Patrick's concept of the mechanism of adsorption and heat of wetting emphasizes the idea of the attractive force between the molecules of the liquid as manifested in surface tension; the older concept emphasizes the attractive force between the surface molecules of the adsorbent and the molecules of the liquid. But according to either hypothesis, differences in the kind of surface presented by the adsorbent and differences in the extent of adsorbing surface should both produce differences in the heat of immersion in a given liquid.

Soil colloids, like silica gel, contain considerable water not driven off at 110° C.[11] If it were assumed that the ultimate particles of all soil colloids possess water surfaces and are constituted similarly to silica gel, then the heats of wetting of the different colloids should be proportional to the capillary surfaces exposed. The total surfaces or the average diameter of the capillaries would depend on the average size of particles. On these assumptions, the heats of wetting of the different colloids should show a relation to the average size of particles.

If the different soil colloids, which vary widely in chemical composition, possess different kinds of surfaces prior to immersion, then the heats of wetting may be expected to reflect the influence of both extent and nature of the surface. In this case the heats of wetting of various colloids should show some relation to the size of particles and some relation to other factors which are particularly dependent upon the nature of the surface.

It is, of course, very probable that the area or size of the particles is intimately associated with, or dependent upon, the kind of surface; that is, upon the nature of the boundary layer of the colloid particle or micelle. If a surface with a great attraction for water were associated with small particle size, greater differences might be expected in the heats of wetting of the different colloids than in the average size of particles. If, on the other hand, the relation between kind of surface and size were the reverse, smaller differences might be expected in the heats of wetting than in the average size of particles.

The heat of wetting in water was determined for colloidal materials extracted from eight different soils. These values are given in Table 4. The determinations were made by immersing the samples in water after drying for 18 hours at 110° C. without outgassing.[12] Details of the procedure are given in a previous publication (*2*).

[11] It has been shown that soil colloids contain from 3 to 16 per cent of water not driven off at 110° C. (*47*).

[12] An attempt was made to obtain the heat of wetting on outgassed material, as it was thought that this might form a better basis for comparing the different colloids. Experimental difficulties were encountered, however, in working with certain highly plastic colloids. It is possible that the heats of wetting of evacuated colloids might have been higher in some cases, although no evidence to this effect was obtained.

TABLE 4.—*The heats of wetting of colloidal soil materials*

Kind of colloid	Heat of wetting per gram of colloid	Kind of colloid	Heat of wetting per gram of colloid
	Calories		*Calories*
Fallon	17.5	Huntington	8.3
Sharkey	16.3	Aragon	8.0
Marshall	14.6	Norfolk	7.6
Sassafras	9.8	Susquehanna	5.3

The heats of wetting of the different colloids vary from 5.3 to 17.5 calories per gram. The higher values are of the same order of magnitude as Patrick (*44*) found for silica gel (19.2 calories per gram) and as Harkins (*23*) gives for bone charcoal when immersed in water (18.3 calories per gram).

If the same assumptions are made for the soil colloids as Patrick made for silica gel, the diameters of the particles in the different colloids would range from 3.6 millimicrons for the Fallon colloid to 12 millimicrons for the Susquehanna colloid. These diameters are only about one-tenth those shown by the Zsigmondy count method. The values obtained by the Zsigmondy method seem more probable. However, the values derived by assuming an application of Patrick's hypothesis are not beyond the range of possibility, for it must be borne in mind that many of the particles counted may in reality have been aggregates.

It is of course doubtful whether Patrick's hypothesis leads to absolutely true conclusions regarding the size of silica-gel particles, for he points out in a subsequent paper that the values deduced seem too small in the light of other data on silica gel (*45*). It is also doubtful whether Patrick's hypothesis regarding silica gel should be applied in its entirety to soil colloids; particularly since the difference between heat of wetting in organic liquids and heat of wetting in water is greater for silica gel than for soil colloids. According to Patrick and Grimm (*44*), the heats evolved by silica gel in benzene and in alcohol are respectively 0.58 and 1.18 times the heat evolved in water. On the other hand, the Fallon and Sassafras colloids evolve only 0.36 and 0.40 as much heat in benzene as in water and 0.84 and 0.78 as much heat in alcohol as in water.

Aside from theoretical considerations, a correspondence obviously exists between particle size and heat of wetting. The data given in Tables 2 and 4 show that the heat of wetting tends to increase with decreasing particle size as determined by the Zsigmondy count method, and is roughly proportional to the number of particles per gram of material or inversely to the average volume of a single particle.

ADSORPTION OF VAPORS

Adsorptive capacity has generally been regarded as one of the most characteristic properties of colloidal soil material. In fact, several methods for determining the quantity of colloid in a soil or clay have been based upon this property (*41*, *20*, *4*, *46*). It has been recently shown that the colloidal materials extracted from different soils may vary widely in adsorptive capacities (*20*). The different soil col-

loids may therefore be partially distinguished by their adsorptive capacities. Since the adsorption of gases and vapors is considered by many to be a somewhat different type of phenomenon from that of the adsorption of electrolytes, the capacities of the colloids for adsorping vapors and electrolytes will be considered separately.

Many theories have been evolved regarding the mechanism of the adsorption process and regarding the characteristics of the materials which may be responsible for this phenomenon. According to adsorption theories, the quantities of a given vapor adsorbed by different solid adsorbents would depend on the extent of the surface exposed in submicroscopic capillaries and also on the specific adsorbing power of the surface (the nature of the surface). However, estimations free from assumptions for either of these values are lacking in the case of highly adsorptive materials. Some adsorbents, such as charcoal and silica gel, give little evidence of specificity in adsorbing vapors, the quantities of different vapors adsorbed by a given preparation frequently following approximately the condensabilities of the vapors (*14*). According to one theory, the quantities of vapor adsorbed by such adsorbents are regarded as indicative of the volumes of the submicroscopic capillaries, the limits of whose diameters do not exceed a certain magnitude. There are, however, many instances where the specific nature of the surface appears to determine the quantity of gas adsorbed far more than does the estimated volume of the capillaries or the extent of the surface.

The adsorptive capacity of colloidal soil material for a series of vapors has not been determined; hence it is not known whether this material adsorbs vapors in the order of their condensabilities or whether the specific nature of the surface significantly affects adsorption. The unlike chemical compositions of the different soil colloids suggests that they may present different kinds of surfaces to a vapor and may therefore be specific in their adsorptions. On the other hand, many adsorbents of very unlike chemical composition, such as charcoal, platinum black, and silica gel, show little specificity in adsorption.

A complete picture of the differences in adsorbing power for vapors exhibited by the various soil colloids would involve determinations of the adsorption of a variety of vapors under different conditions. Such a detailed study was beyond the scope of this investigation. This bulletin gives only the quantities of ammonia and water vapors adsorbed at a single temperature and pressure.

The adsorption of ammonia was determined by the method described in a recent publication of this bureau (*20*). The vapor was maintained at 1 centimeter above atmospheric pressure and the temperature of adsorption was 0° C. The quantity of adsorbed ammonia determined was not the total quantity adsorbed by the colloid, but was that portion of the total adsorbed at 0° C., which was liberated at 100° C. by passing a current of air over the samples.[13]

The adsorption of water vapor was conducted in an evacuated desiccator over 30 per cent sulphuric acid at 30° C. This procedure was essentially the same as that described in a previous publication (*20*), except that previously 3.3 per cent (by weight) sulphuric

[13] Determinations made by H. E. Middleton showed that about 15 per cent of the total quantity of ammonia adsorbed by soil colloids was retained after the vapor had been driven off at 100° C. by aspiration.

acid was used.[14] After equilibrium was reached in the desiccator, the samples were dried for 18 hours at 110° C., and the loss in weight was taken as the quantity of water adsorbed.

Table 5 shows the quantities of water and of ammonia adsorbed by seven soil colloids and the relation between the adsorption of the two vapors.

TABLE 5.—*Adsorption of water and ammonia vapors by soil colloids*

Kind of colloid	H_2O adsorbed per gram of colloid[1]	NH_3 adsorbed per gram of colloid	Ratio $\frac{H_2O \text{ adsorbed}}{NH_3 \text{ adsorbed}}$
	Gram	*Gram*	
Fallon	0.1776	0.0532	3.34
Sharkey	.1605	.0529	3.03
Marshall	.1305	.0415	3.14
Sassafras	.1143	.0264	4.33
Aragon	.0886	[2]	
Norfolk	.0845	.0266	3.18
Huntington	.0633	.0214	2.96
Susquehanna	.0518	.0177	2.93

[1] Determinations made by H. E. Middleton. [2] Not determined.

There is a considerable range in the adsorptive capacities of the different colloids for water vapor and for ammonia, the most adsorptive colloid of the series taking up approximately three times as much water or ammonia as the least adsorptive material.

It is evident from the last column that the quantities of ammonia adsorbed by the different colloids are, with one exception, approximately proportional to the quantities of water vapor adsorbed under the conditions of the determinations. It is thus apparent that, if the colloids possess any specificity for the adsorption of either ammonia or water vapor, they possess, on the whole, the same degree of specificity for both substances.

The fact that the colloids adsorb more water than ammonia is in accord with the capillary theory of adsorption; since under the condition of the determination the corresponding pressure[15] of the water vapor was about three times as great as that of the ammonia (*34*, *54*, *55*). This indicates that the mechanism of the adsorption process in soil colloids is similar to that in such substances as silica gel and charcoal, which frequently adsorb vapors in the order of their corresponding pressure modified by the liquid volumes of the condensed vapors. However, the data for adsorption of soil colloids are too meager to establish this similarity with any surety.

If the mechanism of adsorption were the same in soil colloids as in silica gel, it would be reasonable to assume a similar structure for the two materials. Many hold that inorganic gels are made up of an agglomeration of particles and that capillary spaces are formed

[14] Different soil colloids vary much less in their capacity for adsorbing water vapor from a very humid atmosphere than from a drier one. Strong acid was used, therefore, to bring out differences characteristic of the colloids.

[15] The term "corresponding" presure has been used for expressing the relation $\frac{P}{Po}$ where P is the pressure of the vapor in equilibrium with the adsorbent and Po the saturation pressure of the vapor at the temperature of adsorption. In the case of water vapor under the conditions employed the value for $\frac{P}{Po}$ was 0.75, and $\frac{P}{Po}$ for ammonia was 0.24.

by the juxtaposition of these particles. In such a system the number of capillary spaces of a given diameter would be determined largely by the number of particles of a given diameter. It is interesting to note, in connection with this theory, that the quantities of vapor adsorbed by different soil colloids are roughly proportional to the estimated number of particles per gram.

SWELLING

In 1895 Williams (*56*) called attention to the swelling of his finest mechanical separate of soils as one of the properties distinguishing it from the coarser soil fraction. Tempany (*52*), Hardy (*22*), and others have investigated the swelling of different soils, and Gedroiz (*15*) has studied the swelling of the same soil subject to different treatments. Hardy gives no direct determinations of the swelling of isolated colloids, but he suggests that the colloids from different soils may vary in degrees of swelling.

Swelling might be generally defined as an increase in volume attendant on the taking up of a liquid or vapor. In the taking up of liquids by substances which do not swell, probably essentially the same mechanism is involved as in the taking up of liquids by substances which do swell. The difference in the two cases may lie in that the process does not involve a change in structure of the colloid in the first case, but does involve a progressive alteration in structure in the second case. Freundlich (*14*), for instance, considers that there is no sharp distinction in the mechanism by which the liquid is taken up by elastic and inelectic gels, that is, by gels that do and do not swell.

Ignited or aged silica gel is usually cited as a typical inelastic gel. A granule of this material may take up considerable water with little, if any, change in apparent volume. Thus it does not swell according to the common conception of swelling. It is generally considered that the gel mass is porous and that the liquid taken up is held in the pores, which do not change appreciably in volume during the process. The typical elastic gels on the other hand, of which gelatin is an example, increase in apparent volume as water is added. The dry gelatin gel is usually pictured as a reticular structure of gelatin with interstitial spaces filled with air or liquid. As liquid is taken up, the interstitial spaces expand.

It is usually assumed that when elastic or inelastic gels take up large quantities of a liquid that the liquid occupies approximately its normal liquid volume in the gel. Some hold, however, that the lesser amounts of liquid, such as would be absorbed from a vapor below its saturation pressure, are held under such compression as to quite appreciably diminish the normal liquid volume. It seems that the taking up of liquids by elastic and inelastic gels is very similar. Differences in the quantity of liquid taken up and the manner in which it is held may be of degree only, and may be due chiefly to differences in the size of pores, to differences in rigidity of the gel framework, and to differences in the affinity for the liquid.

In order fully to chara terize a gel by its swelling, it is obviously important to know the quantities of liquids it holds under various conditions and the volume and energy changes accompanying the taking up of the liquids. Various studies by Van Bemmelen (6),

Zsigmondy (*57*), Katz (*28*), Rosenbohm (*48*), and many other investigators have supplied such information for silica gel and gelatin.

It was beyond the scope of this investigation to study all phases of the swelling of the different soil colloids. An attempt was made, however, to determine (1) the volume changes taking place when the colloids were in contact with liquid water, (2) the quantities of water the colloids would imbibe against gravity, and (3) the quantities of water the colloids would hold against 1,000 gravity after they had been in contact with liquid water (moisture equivalent determination) (10). Samples of silica gel, gelatin, and bentonite were included in these determinations in order that the behavior of the soil colloid might be compared with that of well-known colloids.[16] Possibly more light would be thrown on the natures of the different soil colloids by determining the vapor pressures of the colloids with different moisture contents, but it was thought advisable first to make determinations which have a more obvious application to the behavior of soils.

Fischer (*13, p. 44–151*), Loeb (*32*), and others have determined the volume changes of fibrin and gelatin in different solutions by merely measuring the volume occupied by the granulated material in a graduated cylinder containing the solution. This method is doubtless fairly accurate for estimating differences produced in a single material that swells several hundred per cent. Applied to more pulverulent or "sandy" materials, such as the soil colloids, the method is probably only qualitative. In order to estimate variations in the swelling of different materials in the same liquid it is necessary to modify the Fischer method by including a determination of the volumes occupied by the materials in a liquid in which they do not swell. Therefore, in comparing the swelling of different soil colloids with the swelling of silica gel, gelatin and bentonite measurements were made of the volumes occupied by the materials in benzene and in water. It was assumed that the materials did not swell in benzene, and the volumes occupied in this liquid were used as the base on which to calculate the changes in volume, or swelling, in water.

The procedure was as follows: The air-dried colloids were coarsely pulverized and passed through sieves. Only material passing a 1-millimeter sieve and retained on a 0.5-millimeter sieve was used. Samples of 5 grams each were placed in graduated tubes with 15 cubic centimeters of water or benzene. In order to remove air the tubes were evacuated to the boiling point at room temperature. After standing three hours the volume occupied by the colloid was observed.

The observed volume of the colloidal material was, of course, the volume of the colloid lumps plus the volume of the liquid between the lumps. In the process of swelling there was presumably an alteration not only in the size of the lumps, but also in the space between the lumps, although it is assumed in the method that the total pore space between aggregates does not change. Thus

[16] The silica gel used was a commercial product prepared by Patrick's method. The gelatin was a preparation for bacteriological work; it had a pH of approximately 6.0 in water. The bentonite was procured from a company supplying mineralogical specimens; it was a typical sample of this highly colloidal mineral, the characteristics of which are described by Ladoo (*30*).

the increases in volume recorded were probably only indicative of differences in degrees of swelling. It was assumed in the procedure that the various colloids did not swell in benzene. Although this may not be strictly true, it was at least approximately correct for the soil colloids, since the lumps did not break down in benzene as they did in water and no change in volume was apparent under the microscope. In the case of gelatin or bentonite the difference between the volume in water and in benzene was so great that some swelling in benzene would not have affected the comparisons made.

The swelling capacities of the different colloids indicated by this method are shown in Table 6. The magnitude of swelling, given in the last column, is the difference between the volume of the material in water and in benzene, calculated as per cent of the benzene volume.

TABLE 6.—*Swelling (volume increase) of colloids in water*

Kind of colloid	Volume per gram in benzene	Volume per gram in water	Swelling
	Cubic centimeters	*Cubic centimeters*	*Per cent*
Gelatin	1.8	18.0	900
Silica gel	1.1	1.14	4
Bentonite	1.1	9.0	718
Fallon	1.0	2.5	150
Sharkey	1.0	1.9	90
Susquehanna	1.1	2.0	82
Marshall	1.1	1.8	64
Miami	1.1	1.8	64
Sassafras	1.1	1.8	64
Huntington	1.3	1.9	46
Cecil	1.3	1.9	46
Norfolk	1.3	1.8	38

All the materials except silica gel occupied an appreciably larger volume in water than in benzene. The soil colloids swelled more than silica gel but much less than gelatin or bentonite. Thus, with respect to volume changes in water, the soil colloids stand between a typical nonelastic and a typical elastic gel. Probably not much significance should be attached to the smaller differences among the various soil colloids, considering the lack of strict accuracy of the method, but it is safe to conclude that the greatest volume change took place in the Fallon colloid and possibly the least in the Norfolk.

Further light on the volume changes of the different materials was obtained by observing the behavior of separate particles under a low-power microscope. The ignited silica gel remained unchanged in water, and a particle of gelatin slowly increased in size without losing its apparent homogeneity. This, of course, is in accord with the conception of a rigid structure for ignited silica gel and an elastic structure for gelatin. A particle of bentonite increased quickly its volume in water and broke down progressively into a nearly uniform, finely granular mass which apparently had only a slight coherence, since some small aggregates separated from the edges. Bentonite might therefore be regarded as a somewhat elastic gel of a less homogenous and coherent structure than gelatin.

The soil colloids as a class behaved more like bentonite than like silica gel or gelatin, although they all differed somewhat in behavior and none of them resembled bentonite closely. They all broke down suddenly in water into irregular masses of the same general appearance as the original particle. The lumps of Fallon colloid showed least disintegration and the Norfolk showed most. Part of the swelling of the soil colloids recorded in Table 6 may have been due to fractured particles packing less closely than the original lumps, but all the volume increases of certain colloids could not be accounted for in this way. In the case of the Fallon colloid, which swelled most and fractured least, the swelling must have been due chiefly to an increase in volume of the material without any change in homogeneity that was apparent under the low-power microscope. Certain of the soil colloids thus appear to possess some degree of elasticity, though it may be slight.[17]

Hofmeister (*25*) and many subsequent investigators, in determining the quantity of water imbibed by gelatin and similar colloids, merely immersed disks of the material in water, wiped the surface with filter paper, and weighed. Katz (*28*) modified the procedure for pulverulent materials by drying between porous plates. These procedures were not well adapted to soil colloids; hence the following method was devised:

The air-dried colloids were thoroughly mixed with about 25 per cent of water and were then compressed under 3,000 pounds pressure per square inch into cylindrical briquettes 16 millimeters in diameter by approximately 15 millimeters high. The briquettes were placed on a blotter, one end of which dipped into a dish of water, and were left over night covered with a bell jar. In the morning the briquettes were weighed, and after drying at 110° C. for 18 hours they were weighed again, the loss in weight being imbibed water. Some of the briquettes cracked as water was imbibed, but moistening the material prior to briquetting greatly diminished cracking.

The above procedure gives the quantity of water the briquetted colloids will take up and hold against gravity. The quantities of water the powdered soil colloids will hold against a centrifugal force equivalent to 1,000 gravity were determined by the moisture-equivalent method. This method was applied to the soil colloids essentially as Briggs and McLane (*10*) developed it for soils.

Duplicate determinations by either the modified Hofmeister or moisture-equivalent methods usually varied less than 5 per cent when the same lot of colloid was used; but frequently different lots of the same kind of colloid prepared under slightly varying conditions did not agree so closely. Probably the results by both methods are affected somewhat by a state of aggregation of the colloid that is not controlled in the experimental procedures.

[17] Additional data regarding swelling of the colloids were obtained by W. H. Fry through microscopic observation of single lumps. The volume of a single lump before immersion in water was estimated by the aid of an eyepiece micrometer, and the combined volumes of the aggregates into which the single lump broke up in water were also estimated. Volume increases estimated in this way approximated roughly those given in Table 6. The microscopic estimates of swelling were as follows: The Sassafras colloid, 37 per cent; the Sharkey, 87 per cent; and four values were obtained for the Fallon, which ranged from 44 to 193 per cent and averaged 110 per cent. Thus it seems that the volume increases given in Table 6 were largely due to volume increases in aggregates which appeared homogeneous under the low-power microscope and not to such aggregates packing diifferently in water and in benzene.

Table 7 shows the water imbibed by nine soil colloids, silica gel, bentonite, and gelatin in the Hofmeister determination, and the water held by seven soil colloids in the moisture-equivalent determination. The water taken up in each case is expressed as per cent of the dry weight of the material.

TABLE 7.—*Quantities of water held by different colloids*

Kind of colloid	Water held by briquetted material	Water held, moisture equivalent	Kind of colloid	Water held by briquetted material	Water held, moisture equivalent
	Per cent	*Per cent*		*Per cent*	*Per cent*
Gelatin	1,045		Susquehanna	88	67
Silica gel	56		Miami	84	
Bentonite	687		Sassafras	76	62
Fallon	139	120	Norfolk	63	62
Sharkey	123	94	Huntington	60	64
Marshall	101	72	Cecil	48	

The colloids held somewhat more water under the conditions of the briquette test than under those of the moisture equivalent. This was to be expected; since in the briquette method water is held against gravity, whereas in the moisture-equivalent method it is held against a force equivalent to 1,000 gravity. Other differences in the conditions of the methods also are doubtless responsible for part of the difference in results. For instance, the state of aggregation of the colloids on exposure to water was different. Both methods bring out significant differences in the water-holding capacities of the different soil colloids. The briquette method perhaps gives the more accurate comparison of the different colloids, since the materials used in this test were all prepared in as uniform a manner as possible.

The different soil colloids, with the exception of the Susquehanna, vary in their capacities for holding liquid water almost exactly as they vary in their capacities for adsorbing water vapor over 30 per cent sulphuric acid. (Table 5.) Each colloid held approximately 7.5 times as much water in the briquette test as in the adsorption test over 30 per cent sulphuric acid. Also, the quantities of water held by the different colloids are nearly proportional to the heats evolved on wetting. The correspondence between these determinations for a series of soil colloids is shown in Table 8 by means of three ratios.

TABLE 8.—*Proportionalities between water-holding capacity, water-vapor adsorption, and heat of wetting of soil colloids*

Kind of colloid	Water imbibed by briquettes divided by water-vapor adsorbed	Water imbibed by briquettes divided by heat of wetting	Heat of wetting divided by water-vapor adsorbed
Fallon	7.9	7.9	99
Huntington	9.5	7.2	131
Marshall	7.7	7.0	112
Norfolk	7.5	8.3	90
Sassafras	6.6	7.9	86
Sharkey	7.7	7.5	102
Susquehanna	17.0	16.6	102

Each of these determinations—quantity of liquid water held, water vapor adsorbed over strong sulphuric acid, and heat of wetting—may be regarded as a measure of some phase of the affinity of the material for water. The correspondence between the different determinations, shown by the constancy of the ratios in Table 8, indicates that in the case of most soil colloids any one of these determinations is sufficient for characterizing the affinity of the material for water.

Some light is thrown on the nature of the soil colloids by comparing the quantities of water held (Table 7) with the volume changes (Table 6) of the different materials. Gelatin and bentonite hold large quantities of water and increase in volume in proportion to the water held. The inelastic silica gel holds much less water than these materials and shows practically no volume change. Nearly all the soil colloids hold somewhat more water than silica gel. The Fallon, Sharkey, and Marshall colloids hold approximately twice as much, and they increase in volume markedly. The volume increase in the case of the Fallon and Susquehanna colloids is approximately equal to the weight of water held; in the case of the other soil colloids it is 0.6 to 0.8 of the weight of water held. On the basis of these results the soil colloids might be regarded as elastic gels. But in view of the fact that all the soil colloids showed more or less fracturing under the microscope, probably none of them should be considered typically elastic gels.

VISCOSITY

The viscous behavior of a colloid has long been considered especially important for characterizing the general nature of the material. At low concentrations the lyophile colloids are much more viscous than the lyophobe, and the critical concentration at which a sharp increase in viscosity occurs is usually much lower for the typical lyophile than for the typical lyophobe colloids. As a rule the viscosity of the lyophiles is more affected than that of the lyophobes by changes in temperature, manipulation, time of standing, and the like.

Although colloids are characterized by their viscous behavior, viscosity apparently can not be considered the expression of a single, definite property of a colloid, such as size of particle. Although viscosity seems to be largely determined by the volume of the dispersed phase in proportion to the volume of the dispersion medium, few sols follow exactly Einstein's formula (*12*) for increase in viscosity with increasing volume concentration. It has usually been assumed that deviations from this formula are due to liquid which is associated with the dispersed phase so closely that it acts as a part of the solid volume of the dispersed phase in so far as viscosity is concerned. Aggregation and variation in electrical charge seem to affect the viscosity, presumably by affecting the volume of the associated liquid. According to Odén's (*42*) investigations of sulphur sols, size of particles also influences viscosity.

The viscosity of the soil colloids was determined with an Ostwald pipette of such dimensions that 25 cubic centimeters of water was delivered in about 60 seconds. Determinations were made at 25° C. and could be duplicated within 0.4 second if the sol did not stand

too long. In order to overcome the changes that some sols undergo on standing, and to have the different colloids in a comparable condition for testing, the sols were drawn through a Gooch crucible several times just before making the viscosity determination.

Determinations were made of suspensions in pure water and in water containing a few drops of ammonia to promote dispersion. All suspensions contained the equivalent of 2 grams of oven-dried colloid per 100 grams of suspension. The results obtained are shown in Table 9. The viscosity is expressed as the viscosity ratio, which is the viscosity of the colloid compared with that of pure water at the same temperature.

TABLE 9.—*Relative viscosity of soil colloids*

Kind of colloid	Relative viscosity of untreated colloid	Relative viscosity of colloid treated with ammonia	Kind of colloid	Relative viscosity of untreated colloid	Relative viscosity of colloid treated with ammonia
Fallon	1.33		Huntington	1.16	1.14
Sassafras	1.33	1.08	Sharkey	1.14	1.13
Susquehanna	1.27	1.04	Norfolk	1.12	1.00
Marshall	1.23		Aragon		1.05

The viscosities of the different soil colloids vary considerably. These variations could not be due to differences in solid volume, since the sols all contained the same quantity of solid material and the densities of the different colloids were essentially the same. According to the theory of Einstein, the viscosities of colloids at equal volume concentrations should be the same, provided the particles behave as rigid spheres. Variations from this formula have frequently been explained by assuming the association of water with the particles, the quantity of associated liquid being influenced by particle size, by condition of aggregation, and perhaps by other factors.

In the case of the soil colloids, the viscosities showed little or no relationship to average particle size. It seems probable, however, that the viscosities of the different colloids were largely dependent upon the state of aggregation. The data in Table 9 suggest this. A comparison of columns 2 and 3 show that somewhat lower viscosities were obtained when the colloids were dispersed in water to which a little ammonia had been added to promote deflocculation than when pure water was used. Furthermore, the acid colloids, the Susquehanna, Sassafras, and Norfolk, which were difficult to disperse in pure water, were much more affected by the addition of ammonia than were the neutral or alkaline colloids, which were easily dispersed in pure water.

One of the characteristic differences between lyophile and lyophobe colloids is the difference in the concentration at which they become exceedingly viscous. This suggests that the different colloids might be compared on the basis of the concentration required to give a high viscosity, as well as on the basis of their viscosities at a given concentration. The seven soil colloids were therefore compared on this basis.

An Ostwald type pipette was not well adapted for the determination of the viscosity of concentrated soil colloids, since the material adhering to the glass obscured the flow; hence use was made of a 100 cubic centimeter pipette which had an opening of such size that 50 cubic centimeter of water was delivered in about 18 seconds. The pipette was placed in an air thermostat at 25° C. and filled to the mark. The time required to deliver 50 cubic centimeters into a graduated flask was noted. The sols were prepared in the same manner as the dilute sols, no deflocculating agent being used.

Determinations were made of suspensions containing varying concentrations of solid. It was found that, after a concentration sufficient to give a relative viscosity of 1.4 was reached, the viscosity increased very rapidly with a slight increase in concentration. At a relative viscosity just above 2 the flow became irregular. A further slight increase in concentration apparently brought the colloids into the region of zero fluidity, which Bingham (7) suggests is where true viscous flow ceases and plastic flow begins. The different colloids were therefore compared on the basis of the concentrations required to give a relative viscosity of 1.9, which was about the highest point where viscosity could be determined accurately with the particular pipette used.

Table 10 shows the grams of colloid per 100 grams of suspension which were required to give a relative viscosity of 1.9 with the particular pipette employed.

TABLE 10.—*Concentrations of soil colloids required to produce a relative viscosity of 1.9*

Kind of colloid	Concentration of solid	Kind of colloid	Concentration of solid
	Per cent		*Per cent*
Fallon	11.2	Marshall	13.8
Susquehanna	11.9	Norfolk	16.4
Sassafras	13.1	Huntington	19.0
Sharkey	13.8		

Judging from the concentrations at which the soil colloids approach zero fluidity, they are evidently not markedly lyophile, as compared with starch, gelatin, and agar, which under certain conditions form jellies at concentrations of 0.5 to 2 per cent (*49*).

There is considerable variation in the concentrations at which the different soil colloids have a relative viscosity of 1.9. These variations do not parallel differences in the viscosity of 2 per cent suspensions, but they show some correlation with swelling as measured by either the volume or weight methods. A parallelism between viscosity and swelling has previously been observed in the case of several other colloids (*33*, *43*).

VOLUME OF FLOC

Different sols have often been characterized in a general way by the conditions or reagents producing flocculation. Comparative sensitiveness to electrolytes, for instance, is one of the more important criteria recognized as distinguishing lyophobe from lyophile col-

loids. Little attention, however, has been paid to comparative volumes of the coagulated materials. Doubtless such comparative volumes are without much significance in the case of widely different soils, but in the case of closely related materials, such as colloids isolated from different soils, the volumes of floc may be characteristic of the colloidal materials.

It was not the purpose in these studies to investigate the factors influencing the coagulation of the different colloids, but merely to coagulate them in a comparable manner so that differences in flocculated volumes would be as nearly as possible characteristic of the materials. The procedure was as follows: Sols containing 3 to 5 grams of solid per liter were prepared from soil colloids that had not been air dried after isolation from the soil. Sufficient methylene blue to produce rapid flocculation was added to a quantity of the sol containing 0.2 gram of solid, and the volume was made to 100 cubic centimeters. The solutions were well mixed by shaking and were poured into graduated tubes of identical dimensions. At the end of 24 hours the volumes occupied by the flocculated colloids were observed. Preliminary tests were made to determine the quantity of methylene blue needed to flocculate rapidly each colloid. In most cases the methylene blue needed was proportional to the quantity required for rendering isoelectric the more dilute sols employed in the work on cataphoresis (p. 29).

The volumes occupied by seven soil colloids flocculated by the above procedure are given in Table 11. The relation of the volume of floc to the number of particles present in the unflocculated sol is also shown in columns 3 and 4.

TABLE 11.—*Volume of floc and number of particles per gram of colloid*

Kind of colloid	Volume of floc per gram of colloid	Number of particles per gram divided by 10^{12}	$\frac{\text{Number particles per gram}}{\text{volume floc} \times 10^{12}}$
	Cubic centimeters		
Fallon	128	680	5.3
Sharkey	110	960	8.7
Marshall	58.5	613	10.5
Sassafras	38.0	335	8.8
Huntington	31.5	505	16.0
Norfolk	31.0	322	10.4
Susquehanna	31.0	263	8.5

The different colloids vary widely in volume of floc, the Fallon giving a volume four times as great as the Norfolk or Susquehanna. Differences in volume are evidently more or less characteristic of the colloids, since it is apparent from column 4 that there is some correspondence between volume of floc and number of particles in the suspension as determined by the Zsigmondy count method.

The correspondence between volume of floc and number of particles would naturally suggest that the volume is a function of the number of particles. It is possible, however, that the numbers of particles in the suspensions used for flocculation were not the same as, or proportional to, the number of particles counted in the dilute sols used to

determine particle size (page 4). Factors determining the volume of floc have been studied so little that it is not known just what the comparative volumes of different colloids indicate concerning the nature of the materials. It seems evident from the data in Table 11, however, that this simple determination may be used to distinguish roughly different kinds of soil colloids.

ADSORPTION OF ELECTROLYTES

The adsorption of vapors by soil colloids has been discussed on page 10. According to certain theories, this type of adsorption is conditioned primarily by the pores of the material. The adsorption of ions from solution, although not unaffected by size of pores or by surface exposed, is coming to be considered more as a chemical reaction taking place at the surface than as a distinctly physical action. A recent article by Michaelis discusses this view of adsorption (*38*).

Some data are available concerning the adsorptive capacity of the isolated colloidal soil material for electrolytes, but there is no information on the adsorption of nonelectrolytes from solution. A previous publication shows that some soil colloids adsorb six times as much malachite green as others; (*20*) and Kelley and Brown (*29*) have shown that colloids extracted from three different soils adsorb different quantities of NH_4 from an NH_4Cl solution.

There is much information in the literature on the capacity of the whole soil for absorbing inorganic salts and dyes from water solution, although very little is known about the absorption of nonelectrolytes. Since it has been shown that practically all of the adsorption of the soil is due to the colloidal material (*1*, *29*), many of the facts established for the whole soil may be taken as applying to the colloid.

The following facts concerning the adsorption of eletrolytes by the colloidal soil material may be taken as established by investigations conducted on the whole soil: (1) Anions, such as Cl, NO_3, SO_4, etc., are adsorbed little, if at all, from salt solutions; (2) the quantity of cation adsorbed increases with the concentration of the solution, approximately as expressed by Freundlich's well-known formula; (3) when a cation is adsorbed an approximately equivalent quantity of other cations is released to the solution.

It is thus apparent from the work on soils that the colloidal soil material has a considerable capacity for the polar type of adsorption, or, as it is commonly called, for "base exchange." However, as the earlier work was conducted on soils which contained undetermined quantities of colloidal materials of unknown compositions, it is not evident from the earlier work just how much the different colloidal soil materials vary in their capacities for exchange adsorption with inorganic salts nor just what part of the bases in the colloidal material are capable of exchange. This information is obviously needed to characterize the different soil colloids and to throw light on the condition of the basic constituents of the material.

Six soil colloids were therefore tested to determine their comparative adsorptive capacity for the same inorganic salt solution, and to determine what part of each base in the colloid exchanges with the base of the salt solution. In base-exchange investigations of soils, ammonium chloride solutions have probably been used more than

other salt solutions, so it was selected for this work. The procedure followed was similar to that employed by Gedroiz (*17*), Hissink (*24*), and Kelley and Brown (*29*). Approximately 15 grams of the colloid were digested overnight with 250 cubic centimeters of a normal ammonium chloride solution at 35° C. After filtering, the colloid was washed with sufficient normal NH_4Cl solution to give a total filtrate of 1,000 cubic centimeters. The filtrate was analyzed to determine the quantities of Ca, Mg, K, and Na that had been removed by the NH_4Cl solution. Since it has been repeatedly shown that the NH_4 adsorbed is practically equivalent to the base removed, the NH_4 adsorbed was not determined, but was assumed to be the same as the total equivalents of monovalent and divalent bases removed. This assumption is not correct for acid colloids, which exchange H or Fe and Al in addition to the monovalent and divalent bases. However, values calculated on this assumption gave a rough comparison of the adsorptive capacities of the colloids for ammonium ions.

Table 12 shows the total quantity of Ca, Mg, K, and Na removed from the different soil colloids by treatment with normal NH_4Cl solution, the quantity being expressed as milliequivalents per gram of colloid. In the third column the quantity of NH_4 that would be adsorbed in replacing these bases is expressed as quantity of NH_3 per gram of colloid. The fourth column gives the quantity of dry NH_3 gas adsorbed by the dry colloid, the figures being taken from Table 5.

TABLE 12.—*Quantity of NH_3 adsorbed from NH_4Cl and from dry ammonia vapor by soil colloids*

Kind of colloid	Ca+Mg+K+Na removed by NH_4Cl from 1 gram of colloid	NH_3 that would be adsorbed from NH_4Cl by replacing Ca, Mg, K, and Na from 1 gram of colloid	NH_3 gas adsorbed by dry colloid per gram
	Milliequivalents	*Gram*	*Gram*
Fallon	1.08	0.0184	0.0532
Sharkey	.69	.0117	.0529
Marshall	.53	.0090	.0415
Sassafras	.23	.0039	.0264
Norfolk	.09	.0015	.0266
Susquehanna	.09	.0015	.0177

It is apparent that the different colloids vary widely in the total equivalents of exchangeable monovalent and divalent bases they contain. They seem to vary more in this constant than in particle size, heat of wetting, swelling, volume of floc, etc. The variation is about of the order previously found in the adsorptive capacity for malachite green (*20*), which is also a base-exchange reaction. Possibly the total equivalents of exchangeable monovalent and divalent bases might be regarded as more nearly a chemical constant than properties previously discussed.

The quantity of NH_4 ions adsorbed by the colloid was not determined directly, but this can be calculated approximately from the milliequivalents of Ca, Mg, K, and Na brought into solution. It is interesting to note that the adsorption of NH_4 ions from NH_4Cl solu-

tion (column 3) was much less in each case than the adsorption of NH_3 from the gas,[18] although the two series of values stand in about the same order. There is of course no reason why there should be any fixed proportion between these two values, since the exact quantity of NH_3 adsorbed from NH_4Cl or from ammonia gas is governed largely by the conditions of the determinations.

If the adsorption of NH_3 from NH_4Cl is primarily a chemical phenomenon and the adsorption of NH_3 gas is chiefly governed by the structure of the colloid, the relation between the two adsorptions might be taken as indicating that structure and chemical activity usually vary in the same direction in the soil colloids, the structure varying less widely than the chemical properties.

Some investigators who worked with the whole soil apparently believed that all the monovalent and divalent bases in the colloidal material are replaceable. Others believed that calcium is replaced to a greater extent than the other bases. Quantitative data bearing on this question are given in Table 13. This table shows the total quantities of the monovalent and divalent bases in the colloid, the quantities removed by the NH_4Cl solution, and the proportion of each base which was removed.

TABLE 13.—*Monovalent and divalent bases present in soil colloids and quantities removed by normal NH_4Cl solution*

Kind of colloid	CaO			MgO			K_2O			Na_2O		
	Present in colloid	Quantity removed	Proportion of total removed	Present in colloid	Quantity removed	Proportion of total removed	Present in colloid	Quantity removed	Proportion of total removed	Present in colloid	Quantity removed	Proportion of total removed
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Fallon	2.36	2.13	90	5.32	0.34	6	2.24	0.34	15	0.54	0.25	46
Sharkey	1.48	1.33	90	2.54	.36	14	1.86	.10	5	.24	.04	17
Marshall	1.12	1.00	89	1.95	.29	15	2.07	.13	6	.19	-------	-------
Sassafras	.37	.39	100	1.37	.13	9	1.04	.04	4	.31	.05	16
Norfolk	.28	17	61	.46	.06	13	.55	Trace.	-------	.31	Trace.	-------
Susquehanna	.18	.13	72	.39	.06	15	.92	.02	2	.29	.02	7

None of the monovalent or divalent bases appear to be completely removable by NH_4Cl. However, there is a wide difference between the bases with regard to the proportion removable. Calcium is nearly all removed from most colloids, whereas only a small part of the magnesium, potassium, or sodium is attacked. The proportion of the total quantity of a base which is removable does not appear to be the same for the different colloids, nor does the absolute quantity of any base which is removable appear to be constant for all colloids, nor does the proportion of a base which is removable appear to vary with the total content of that base.

The quantity of a base which is removable by a neutral salt solution varies somewhat with the nature and concentration of the salt.

[18] In the case of the acid colloids—Norfolk, Sassafras, and Susquehanna—the difference between NH_3 adsorbed from NH_4Cl and from NH_3 gas is somewhat less than is shown in Table 12. Treatment of these colloids with NH_4Cl doubtless exchanged some H or Fe and Al, besides the Ca, Mg, etc., from which the absorption of the NH_3 was calculated. Determinations of the Norfolk colloid, for instance, showed the adsorption of NH_3 from NH_4Cl was approximately 0.0030 gram instead of 0.0015 gram.

But it has been shown that the quantity removed by normal NH_4Cl in the procedure followed in this work is fairly definite and near the maximum removable by neutral salt solutions from the whole soil (*16*, *29*). It seems apparent, therefore, that at least the magnesium, potassium, and sodium present in the colloidal soil material are present in two conditions. Until more is known about the constitution of the colloid the two kinds or conditions of magnesium, etc., may be defined simply by the facts as exchangeable and nonexchangeable.

Although the absolute quantity of any exchangeable base varies widely in different colloids, the proportion of one exchangeable base to another is fairly uniform. The proportionality between equivalents of exchangeable bases is shown in Table 14.

TABLE 14.—*Equivalents of Ca, Mg, K, and Na in 100 equivalents of monovalent and divalent bases exchanged*

Kind of colloid	Ca equivalent	Mg equivalent	K equivalent	Na equivalent	$\frac{Ca+Mg}{K+Na}$	$\frac{Ca+Mg}{Na}$
Fallon	70.4	15.5	6.7	7.4	6.1	11.6
Sharkey	69.0	26.1	3.0	1.9	19.4	50.1
Marshall	67.6	27.3	5.1			
Norfolk	67.0	33.0	Trace.	Trace.		
Sassafras	61.2	28.2	3.5	7.1	8.5	12.6
Susquehanna	52.9	34.5	4.6	8.0	6.9	10.9

In these six colloids, Ca constituted 53 to 70 per cent of the total equivalents of bases exchanged, while the absolute quantity of Ca exchangeable in the different colloids (Table 13) varied between 0.13 per cent and 2.13 per cent CaO. Why there should be a tendency to uniformity in the proportion of the various exchangeable bases has not been explained, although Hissink (*24*), and Kelley and Brown (*29*) have obtained similar results in work on the whole soil, and have suggested that the relative proportions of the bases determine the properties of the colloid. According to Hissink, the properties of the colloid are influenced by the proportions between exchangeable divalent and monovalent bases. Kelley and Brown suggest the ratio $\frac{Ca+Mg}{Na}$ as a determining factor in properties. These two ratios are shown for the different colloids in Table 14.

In the case of these six colloids the adsorptive properties, heat of wetting, swelling, etc., do not correlate well with the ratios proposed by Hissink or by Kelley. Apparently, in the case of these widely different colloids, the properties are dependent more on other chemical characteristics, which will be discussed later, than on the proportions of the exchangeable bases. Considering the low accuracy with which the quantity of sodium can be determined in a normal ammonium chloride extract of a soil, this ratio obviously may not be very accurate in the case of soils containing small quantities of exchangeable sodium. It is, of course, probable that within general types of soil the properties of the different colloids may correlate well with the proportions of the exchangeable bases, as found by Hissink and by Kelley.

Gedroiz *(15, 18, 19)* has shown that the dispersability of the colloid and the swelling of a soil are markedly affected by altering the kind of exchangeable bases present by treatment with neutral salts. The introduction of sodium into the colloid, for instance, gives a far greater dispersion than the introduction of calcium. Thus it would appear also from Gedroiz's work that the physical properties of the colloid should be determined by the relative proportions of the bases. The correlation between properties and relative proportions of bases would probably be more apparent in the case of colloids containing approximately the same quantity of total exchangeable bases, than in the case of these six colloids, which contain widely different quantities.

It has already been shown in Table 12 that there is a fair degree of parallelism between the total exchangeable bases and the adsorption of ammonia vapor, which in turn follows fairly well other properties of the colloid. Inasmuch as there is some uniformity among the different colloids regarding the part of the bases which is present in exchangeable form, it follows that there should also be some parallelism between properties and total content of nonexchangeable monovalent and divalent bases.

Table 15 shows the quantities of the bases which are present in exchangeable and nonexchangeable forms in the six colloids.

TABLE 15.—*Exchangeable and nonexchangeable monovalent and divalent bases in soil colloids*

Kind of colloid	Ca		Mg		K		Na		Total exchangeable bases	Total nonexchangeable bases
	Exchangeable	Nonexchangeable	Exchangeable	Nonexchangeable	Exchangeable	Nonexchangeable	Exchangeable	Nonexchangeable		
	Milliequivalents	*Milliequivalents*	*Milliequivalents*	*Milliequivalents*	*Milliequivalents*	*Milliequivalents*	*Milliequivalents*	*Milliequivalents*	*Milliequivalents*	*Milliequivalents*
Fallon	0.760	0.082	0.168	2.470	0.072	0.403	0.080	0.094	1.080	3.049
Sharkey	.474	.054	.179	1.081	.021	.374	.013	.055	.687	1.574
Marshall	.357	.042	.144	.823	.027	.412			.528	1.277
Sassafras	.139	None.	.074	.615	.008	.212	.016	.084	.227	.911
Norfolk	.061	.039	.030	.198	Trace.	.117	Trace.	.100	.091	.454
Susquehanna	.046	.018	.030	.163	.004	.191	.007	.087	.087	.459

It will be seen that the different colloids stand in the same order when arranged according to the content of either exchangeable or nonexchangeable bases. Properties of the colloid, such as heat of wetting, adsorption of vapors, etc., correlate slightly better with the total exchangeable monovalent and divalent bases than with the content of nonexchangeable bases, but the proportionality is almost as good in one case as in another.

There appears to be more or less of a balance between the total content of exchangeable and nonexchangeable bases. In the case of the Fallon, Marshall, and Sharkey colloids, which are neutral or slightly alkaline, the Ca+Mg+K+Na exchanged fairly represent the total exchangeable bases; and here the total of the nonexchangeable bases is about 2.5 times the total of the exchangeable. In the case of the other three colloids, which are somewhat acid, the Ca+Mg+K+Na exchanged do not quite represent the total exchangeable bases; and here the total of the nonexchangeable bases

is from four to five times that of the exchangeable. If the H or Fe and Al replaced by the salt treatment had been included in the exchangeable bases of these acid colloids, then the nonexchangeable Ca+Mg+K+Na would probably have approximated 2.5 times the total exchangeable bases of the acid colloids also. For instance, data given in a previous paper (*39*, p. 463) show that the total exchange capacities of other samples of the Sassafras and Norfolk colloids were between one-third and one-half as great as the nonexchangeable bases given in this paper. If a balance obtains between exchangeable and nonexchangeable bases, there might be almost as good a correlation between nonexchangeable bases and a property as between exchangeable bases and the given property, although the property might be directly dependent on the exchangeable bases. It would seem from the work of Gedroiz (*15*) that certain properties, such as swelling, may be more directly dependent on the exchangeable bases.

ELECTRICAL CHARGE

The electrical charge of a colloid is an especially important property, since it largely determines the behavior of the material in the sol condition. The sign and magnitude of charge, however, is greatly affected by the medium in which the colloid is dispersed and by the presence of electrolytes. Variations in the charge of particles can readily be followed by measuring the speed with which the particles migrate under the influence of an electric current.

In pure water the colloidal materials from all soils are electronegative. In electrophoresis determinations the particles move toward the anode with a speed of the same order of magnitude as that of the slower ions, the velocity seldom being greater than 3 microns per second under a potential gradient of 1 volt/centimeter.

The charge on the particles of soil colloids is markedly affected by the addition of electrolytes to the water suspensions. Electrolytes might be classed in three groups on the basis of their effects on soil colloids: (1) Electrolytes which in low concentrations increase the negative charge, such as the alkali hydroxides, phosphates, and carbonates; (2) those which even in low concentrations reduce the charge without changing the sign, such as most compounds of the alkaline earths; (3) those which are capable of changing the sign of the charge, such as iron, aluminum, and thorium compounds, the basic dyes and acid gelatin. Although a given electrolyte apparently has qualitatively the same effect on all soil colloids, there are quantitative differences in the action of a given electrolyte on different colloidal soil materials.

The various colloidal soil materials might be characterized with repect to their electrical behavior by differences in the intensity of the negative charge they assume in distilled water and by the quantity of a given electrolyte required to reduce the charge to a given value. Determinations of this kind are readily made by cataphoresis. Inasmuch as the isoelectric point is a critical point in the behavior of colloids, the different soil colloids were compared on the basis of the quantities of an electrolyte required to bring them to electrical neutrality. Obviously only an electrolyte of Group 3 could be used for this purpose, and preliminary tests showed methylene blue was satisfactory.

In determining the quantity of methylene blue [19] required to render each colloid isoelectric, the procedure was as follows: To each of about 10 tubes, 25 cubic centimeters of a suspension containing 10 milligrams of a freshly prepared colloid was added. Varying quantities of methylene blue dissolved in 25 cubic centimeters of water were then added to each tube, and after mixing, the tubes were allowed to stand 24 hours. The following day the tubes were shaken and the cataphoretic movement of the particles or flocs was observed.

The apparatus used for measuring the cataphoretic movements was essentially of the same construction as the one already described by one of the writers, (*36*), the only important changes being that in this experiment the tube was provided with glass stop cocks and that the plane surface under the microscope objective was ground to within 0.2 millimeters of the inner wall, leaving the natural curvature of the latter intact. The optical arrangement was of the Siedentopf-Zsigmondy type. The microscope was focused on a point at a distance of 0.7 of the radius above the axis of the tube. This point lies in an annular layer in which the electrosmotic movement of the liquid in the close tube is theoretically zero, so that observed velocities of the particles in this layer should be their true velocities.

The effect of increasing concentrations of methylene blue on the migration of bentonite and eight colloids is shown in Figure 1. The velocities of the particles are plotted on the ordinate in microns per second for a potential gradient of 1 volt per centimeter. The ordinates also represent the electro-kinetic potential of the particles, since there is a direct proportionality between velocity and charge.[20]

The range over which the colloids were completely flocculated is shown by the broken parts of the curves. There was, of course, partial flocculation preceding this.

Each soil colloid has a characteristic curve, but all the curves are similar in form. After a certain concentration of dye is reached, slight increments affect the charge or movement of the particles profoundly. Flocculation also becomes complete at this point. In the case of bentonite an increased velocity of the particles is produced by a concentration of dye somewhat less than that needed to bring about complete flocculation. The flattening of the curves of the other colloids at this point may be evidence of a similar but less pronounced effect. This phenomenon is common in the case of other colloids but has not been thoroughly explained.

Table 16 shows the migration velocity of the particles in distilled water without any methylene blue, the quantity of methylene blue required to render each colloid isoelectric, and the exchangeable monovalent and divalent bases as determined with an NH_4Cl solution, these last values being taken from Table 12. The quantity of methylene blue required to render 1 gram of colloid isoelectric is expressed in both grams and milliequivalents. Duplicate determina-

[19] The methylene blue used was U. S. P. Medicinal. It contained 13.6 per cent water and 0.48 per cent ash. Calculations were based on the assumption that the balance consisted of tetramethylthionine chloride.

[20] The electro-kinetic potential is calculated from the velocity by the Helmholtz-Perrin formula, $\zeta = \frac{4\pi\eta V 300^2}{H D}$, in which D represents the dielectric constant and η the viscosity of the dispersion medium, V the velocity in centimeters per second, H the potential gradient in volt/centimeters and 300^2 is a constant factor to convert H and ζ to absolute units. Assuming a value of 80 for the dielectric constant and 0.01 for the viscosity of water, ζ, in millivolts, would be obtained by multiplying the microns/second velocities by 14.1.

tions of this quantity were made on four of the colloids and the values agreed with those given in the table within 1 to 2 per cent, showing that they are accurately reproducible provided the set procedure is followed. Strictly speaking, the procedure of determination would show the initial concentration of dye, rather than the quantity of dye, required to render a given concentration of colloid isoelectric. However, in the case of these eight colloids the dye appeared to be completely absorbed at the isoelectric point and somewhat beyond, so the term "quantity" is used with the understanding that it is a fixed value only for the conditions of the procedure. Other experiments showed, however, that the quantity of dye render-

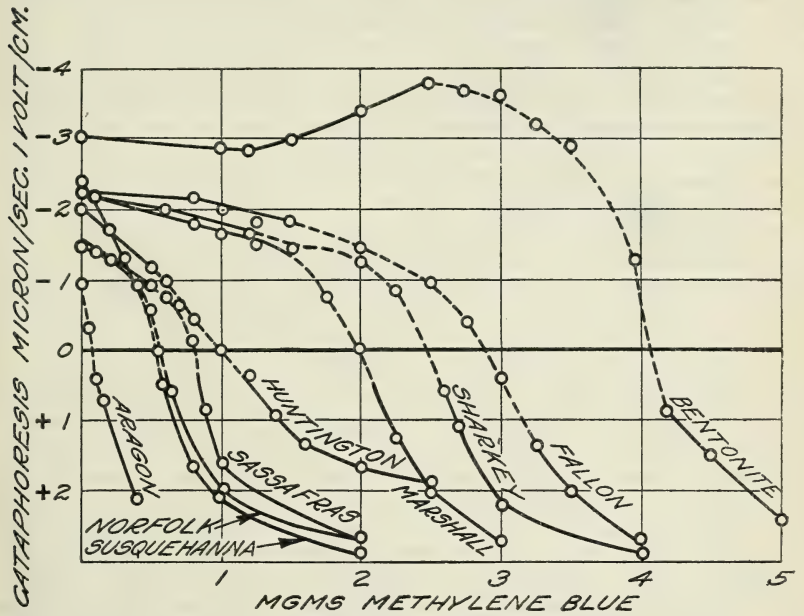

FIG. 1.—Effect of methylene blue on migration of soil colloids

ing 1 gram of the colloid isoelectric did not vary markedly with widely varying concentrations of dye and colloid.

TABLE 16.—*Migration velocity of soil colloids, methylene blue required to render them isoelectric, and content of exchangeable base*

Kind of colloid	Migration velocity of colloid particles in distilled water	Methylene blue required to render 1 gram of colloid isoelectric		Exchangeable Ca, Mg, K, and Na per gram colloid
	Microns	*Gram*	*Milliequivalent*	*Milliequivalent*
Fallon	−2.3	0.287	0.770	1.080
Sharkey	−2.3	.253	.678	.687
Marshall	−2.3	.200	.536	.528
Huntington	−2.0	.100	.268	
Sassafras	−1.6	.082	.220	.227
Norfolk	−1.5	.057	.153	.091
Susquehanna	−2.4	.055	.147	.087
Bentonite	−3.0	.420	1.126	

The velocity of migration of the particles in distilled water apparently does not distinguish the different colloids as well as the quantity of methylene blue required to render them isoelectric. Several different colloids have the same migration velocities in pure water and the range in velocities is less wide than the range in dye values. However, when there is a difference in the migration velocities of the colloids the variations are in the same direction as variations in the dye values, except in the case of the Susquehenna colloid, so that there is some correspondence between the two series of values.

The milliequivalents of methylene blue which render the colloids isoelectric agree fairly well, except in the case of the Norfolk and Susquehanna colloids, with the milliequivalents of Ca, Mg, K, and Na exchanged by the colloid with a normal ammonium chloride solution. In the case of the Norfolk and Susquehanna colloids, the Ca, Mg, K, and Na do not constitute the total quantity of exchangeable bases, since some H or Fe and Al is removed by the NH_4Cl solution, as mentioned on page 24. A comparison of total exchangeable bases and methylene blue required for electrical neutralization shows a close agreement in the case of all these colloids, as pointed out in a previous publication (37).

The correspondence between the methylene blue values and the exchangeable bases, as measured by the ammonium chloride solution, is not surprising, since tests showed that the adsorption of methylene blue by the colloid is also an exchange adsorption. When a 10-gram sample of a Norfolk colloid was treated with methylene blue, 1.32 milliequivalents of the dye were absorbed and 1.36 milliequivalents of bases were displaced. A 2-gram sample of a Sharkey colloid adsorbed 1.01 milliequivalents of the dye, and 1.28 milliequivalents of bases were brought into solution.

The adsorption of methylene blue thus appears to consist in the replacement of equivalent quantities of other bases (Ca, Mg, K, and Na with possibly some H or Fe and Al). Since the methylene blue required to render the colloids isoelectric was completely adsorbed and since this quantity corresponds with the exchangeable base content of the colloid, it is apparent that the colloids were rendered isoelectric when their exchangeable bases were replaced by the methylene blue ion. It is somewhat strange that the substitution of the methylyene blue ion for the exchangeable ions of the colloid should render the colloid electrically neutral: but according to the double-layer theory, as recently discussed by Michaelis (*39*), this might be explained on the ground that the combination between colloid and methylene blue has no tendency to dissociate and form a double layer. This is in accord with the fact that methylene blue appeared to be completely adsorbed, up to the isoelectric point.

The fact that the colloids had negative charges in water varying between 32.4 and 13.7 millivolts[21] when they contained exchangeable Ca, Mg, etc., but had no charge when these bases were substituted by the methylene blue radicle, shows that the charge of the particles is largely influenced by the character of the exchangeable bases. Further evidence that the charge on the particle is largely influenced by the nature of the exchangeable base was obtained by replacing the exchangeable cations in the Susquehanna colloid with Na and

[21] The charge was calculated from the migration velocities as shown on p. 29.

Ca, respectively. The Na-saturated colloid had a charge of 50.7 millivolts in distilled water, while the charge of the Ca-saturated colloid was only 15.5 millivolts. This point is discussed in more detail in a recent publication by Mattson (*37*).

Although the character of the exchangeable bases largely affects the electrical behavior of the colloid, the charge of the particles probably does not vary exactly with the proportions of these bases, as determined by the usual base-exchange methods. According to current theory, the charge on a particle is a direct function of the character of the double layer. Anions and the nature of the adsorbing surface are obviously important in their influence on the double layer as well as the cations. Also, while the cations in the double layer are evidently part of the exchangeable bases, it is possible that only parts of the exchangeable bases, as now determined, are present in the double layer at any one time. If this is so, the proportions of the various cations in the double layer are not necessarily the same as the proportions of the exchangeable bases. For instance, the form of the curves obtained in the experiment with methylene blue (fig. 1) shows that the charge of the particles was not greatly affected by the substitution of methylene blue cation until most of the exchangeable bases were replaced. In tests with Na and Ca saturated colloids, the kind of cation in the double layer probably followed the kind of " exchangeable " base, since there was only one exchangeable base present.

HYDROGEN-ION CONCENTRATION

Numerous investigations have shown that the properties of colloids, particularly those of the lyophile type, are markedly affected by variations in the hydrogen-ion concentration of the dispersion medium. It was beyond the scope of this investigation to study the effect of varying hydrogen-ion concentrations upon the various properties of the soil colloids. However, the pH values which the colloids impart to distilled water is apparently more or less characteristic of the different colloids. Determinations were therefore made of the pH values of the different sols. The colorimetric method was used. These are given in Table 17.

TABLE 17.—*Hydrogen-ion concentration of soil-colloid sols*

Kind of colloid	pH	Kind of colloid	pH
Fallon	8.2	Sassafras	5.7
Marshall	7.1	Susquehanna	5.6
Huntington	7.0	Norfolk	5.3
Sharkey	6.9		

The range in hydrogen-ion concentration of the different colloids covers the values shown by most agricultural soils, except the strongly acid ones. There is some degree of correlation between the pH values of the colloids and other properties, particularly the total content of exchangeable monovalent and divalent bases.

The correspondence between total quantity of exchangeable bases and pH is evidently not a causal relation. The pH is obviously

governed more by the kind of replaceable cations present than by the total quantity. Several investigators, including Gedroiz and Kelley and Brown, have observed that when the exchangeable bases of the soil are replaced by sodium the reaction is alkaline and when hydrogen is substituted the reaction is acid. The correspondence between pH and total quantity of exchangeable bases that obtains in the case of the seven colloids studied is probably due to the fact that those colloids which under natural conditions, contain the smaller quantities of total exchangeable cations, usually contain exchangeable hydrogen ions (or iron and aluminum), while the colloids with the higher content of exchangeable cations are usually saturated with the monovalent and divalent bases.

Although no determinations were made which served as a direct measure of the stability of the different sols or the dispersability of the dry colloids, it was evident in working with various soil colloids that the neutral or alkaline colloids were usually more easily dispersed than the distinctly acid ones and formed more stable sols. The dispersability and stability of the colloids, like the pH, is probably influenced by the character of the exchangeable ions. Gedroiz (*19*) and Kelley and Brown (*39*) have observed that the dispersability of colloids from the whole soil is largely affected by the character of the exchangeable cations, a soil saturated with sodium being much more dispersable than one which has been saturated with hydrogen by an acid treatment. One might therefore regard the dispersability of the colloid and the pH as being both influenced by character of the exchangeable cations. However, high pH and high dispersability do not always go along together. A Ca-saturated colloid, for instance, may have a comparatively high pH but be of comparatively low dispersability.

RELATIONS BETWEEN THE PROPERTIES OF SOIL COLLOIDS

Most of the methods described in the previous pages for determining the properties of the colloids are more or less arbitrary, and the values obtained can not be considered as constants in the same sense that the boiling point is a constant of a pure liquid. Also, the determinations given are in some cases very incomplete characterizations of the properties. For instance, the adsorptive capacity of a colloid for water or ammonia vapor is not fully shown by the quantity adsorbed at a single pressure of the vapor. The adsorptive property of each colloid would be better characterized by a curve showing the quantity adsorbed at different concentrations or pressures. It is quite possible for two colloids to stand in one order on the basis of the quantity of water adsorbed at a given partial pressure and stand in a reverse order on the basis of the quantity adsorbed at another partial pressure. However, it was beyond the scope of this investigation to make a detailed study of any one property.

The data which were obtained in this investigation of properties are brought together in Table 18 for convenience in reference. This table also includes some of the data given in previous publications (*2*, *20*).

TABLE 18.—*Summary of properties of soil colloids*

Kind of colloid	Specific gravity in water	Average diameter of particles	Surface per gram of colloid calculated	Number of particles per gram of colloid calculated	Heat of wetting per gram of colloid	NH_3 adsorbed per gram of colloid	H_2O vapor adsorbed over 30 per cent sulphuric acid per gram of colloid	Imbibed water
		Millicrons	*Square meters*		*Calories*	*Gram*	*Gram*	*Per cent*
Fallon loam soil	2.766	102	21.7	680 by 10^{12}	17.5	0.0532	0.1776	139
Sharkey clay soil	2.718	91	24.7	960 by 10^{12}	16.3	.0529	.1605	123
Marshall loam soil	2.627	106	21.7	613 by 10^{12}	14.6	.0415	.1305	101
Sassafras silt loam subsoil	2.748	128	17.0	335 by 10^{12}	9.8	.0264	.1143	76
Huntington loam soil		111	19.9	505 by 10^{12}	8.3	.0214	.0633	60
Norfolk fine sandy loam subsoil	2.708	129	17.1	322 by 10^{12}	7.6	.0266	.0845	63
Susquehanna clay subsoil		141	15.7	263 by 10^{12}	5.3	.0177	.0518	88
Aragon clay subsoil					8.0		.0886	
Cecil clay loam subsoil					4.5	.0192		48
Chester loam soil					7.2	.0293		
Hagerstown loam subsoil					7.9	.0299		
Miami silty clay loam subsoil					11.8	.0358		84
Stockton clay adobe soil					16.3	.0617		
Wabash silt loam soil					17.6	.0614		

Kind of colloid	Moisture equivalent	Volume increase in water	Volume of floc per gram of colloid	Viscosity of 2 per cent sols	Concentration required to give a viscosity of 1.9	Methylene blue required to render 1 gram of colloid isoelectric	Exchangeable Ca+Mg+K+Na per gram of colloid	pH	Malachite green adsorbed per gram of colloid
	Per cent	*Per cent*	*Cubic centimeters*		*Per cent by weight*	*Gram*	*Milliequivalents*		*Gram*
Fallon loam soil	120	150	128	1.33	11.2	0.287	1.080	8.2	
Sharkey clay soil	94	90	110	1.14	13.8	.253	.687	6.9	
Marshall loam soil	72	64	58.5	1.23	13.8	.200	.528	7.1	
Sassafras silt loam subsoil	62	64	38.0	1.33	13.1	.082	.227	5.7	
Huntington loam soil	64	46	31.5	1.16	19.0	.100		7.0	
Norfolk fine sandy loam subsoil	62	38	31.0	1.12	16.4	.057	.091	5.3	
Susquehanna clay subsoil	67	82	31.0	1.27	11.9	.055	.087	5.6	
Cecil clay loam subsoil		46							0.1582
Chester loam soil									.1348
Hagerstown loam subsoil									.1704
Miami silty clay loam subsoil		64							.2096
Stockton clay adobe soil									.4128
Wabash silt loam soil									.3698

Although the data in Table 18 are not sufficient to bring out all differences in the properties of the various colloids, they are sufficient to show that significant relationships exist between the properties. Some degree of relationship between the properties discussed in the preceding pages is to be expected, since these properties doubt-

less are all dependent upon a few more fundamental properties of the colloid, such as size, structure, and chemical nature of the particles. A precise knowledge of these more fundamental properties is lacking, but an idea of the relationships between the properties given in the preceding pages may be gained from the manner in which variations in one property in a series of soil colloids parallel variations in another property. This is shown in Table 19.

TABLE 19.—*Degree to which different soil colloids possess certain properties, as shown by relative values*

Kind of colloid	Reciprocal of average diameters of particles	Heat of wetting	Adsorption of NH_3	Adsorption of H_2O vapor	Imbibed water	Moisture equivalent	Volume increase in water
Fallon	[1] 78	100	100	100	100	100	100
Sharkey	100	90	99	86	80	55	46
Marshall	60	76	67	63	52	17	23
Sassafras	18	37	25	50	20	0	23
Huntington	49	25	10	9	0	3	7
Norfolk	17	19	25	26	4	0	0
Susquehanna	0	0	0	0	35	9	39

Kind of colloid	Volume of floc	Viscosity of 2 per cent sols	Reciprocal of concentration required to give viscosity of 1.9	Methylene blue required to render isoelectric	Exchangeable Ca+Mg+K+Na	pH	Average of properties
Fallon	100	100	100	100	100	100	98
Sharkey	81	10	54	85	60	55	69
Marshall	28	52	54	63	44	62	51
Sassafras	7	100	65	12	14	14	30
Huntington	0	19	0	19	N. D.	59	15
Norfolk	0	0	23	1	0	0	9
Susquehanna	0	71	86	0	0	10	19

[1] As pointed out on p. 5, there is considerable evidence that the Fallon particles are smaller than those of the Sharkey colloid. If this is so, the figure for the Fallon should be 100 and the figures for the other colloids somewhat less than those in this column.

In Table 19 the degree to which the colloids possess various properties is shown by relative values,[22] to facilitate comparison, since the properties were expressed in many different units in the preceding pages, and the colloids vary more widely in some properties than in others. The basis of the relative values in the case of each property is the range in the property exhibited by the seven colloids which were used in most comparisons. The difference between the highest and lowest values found for the seven colloids is taken as 100 for each property. For instance, the adsorptive capacity of the colloid adsorbing most water is assigned a value of 100; the adsorptive capacity of the colloid adsorbing least water is taken as 0; and the adsorptive capacities of the other five colloids are expressed proportionally to this variation of 100. This method of expression gives a uniform basis of values for different properties and makes the ampli-

[22] The relative specific gravities of the different colloids were omitted from this table, since they showed so little correlation with other properties that their inclusion would have tended to obscure the correspondence obtaining between other properties shown in subsequent calculations.

tude of variation between the lowest and highest determinations the same for all properties.

The seven colloids tend to assume about the same order in the various determinations. The Fallon colloid is the highest in all properties, whereas the Norfolk and Susquehanna are the lowest in most determinations. The Sharkey and Marshall colloids are usually above the mean and the Huntington and Sassafras somewhat below the mean. There are several exceptions to this order, the most notable occurring in the viscosity determinations. As pointed out on page 19, there was some ground for believing that these measurements were largely affected by temporary conditions of the samples, as well as by the more fundamental nature of the material.

The parallelism between the variations of the colloids in one property and variations in another property is closer when certain groups of properties are considered. The properties from "heat of wetting" to "volume increase in water," as shown in Table 19 left to right might be regarded as one group of properties (Group 1), since they have to do with the behavior of the dry gel. The properties, "volume of floc" to "concentration required to give a viscosity of 1.9" may be regarded as another group (Group 2), since they are dependent on the behavior of the material in the sol condition. The last three properties constitute a third group in that these properties, according to current theory, are more directly dependent upon the chemical nature of the material than are the other groups of properties.

Within these groups the variations of the colloids in one property parallel variations in another property in a nearly quantative manner. In the case of certain properties this parallelism in variations can be reasonably explained on the ground that both properties are largely determined by the same fundamental characteristic of the colloid. It has already been pointed out, for instance, that the adsorption of water vapor and ammonia gas are probably both governed to a considerable extent by the structure of the material.

All parallelisms in variations of the properties of the different colloids, however, can not be explained on this basis. For instance, one would not expect that a high capacity for the adsorption of electrolytes (high-exchangeable-base capacity) would necessarily accompany a high heat of wetting or a high capacity for imbibing water. These two properties are presumably largely determined by different fundamental properties of the colloid and, as a matter of fact, some artificial colloids which are very high in one of these two properties are very low in the other. In the case of silica gel, for instance, heat of wetting may be high and the exchange adsorption may be very low.

In the case of the soil colloids, however, there is apparently a fair degree of correspondence between variations in nearly all the properties. This might be taken as indicating that in the case of these materials, the more fundamental properties, such as size, structure, and chemical nature of the particles, are usually associated in a certain way. Small size of particles and a particular kind of structure, for instance, may usually accompany a certain chemical composition of the material. Further evidence of this will be discussed later.

Although the correspondence between variations in different properties of the series of soil colloids indicates that the fundamental

characteristics of the colloid are usually associated in a particular way, it appears that there is not an absolute dependence of one fundamental characteristic on another, since there are so many irregularities in the parallelism between properties. Some of these exceptions may be due to incomplete or imperfect methods of determining the properties or behavior of the different colloids, but it is believed that all irregularities could not be explained in this way. Several exceptions to the parallelism between properties have been noted, aside from the data given in Table 19. The Aragon colloid, for instance, gives a heat of wetting about the same as that of Huntington colloid while it requires only one-eighth as much methylene blue to render it isoelectric (Table 18).

Very little information is available in the literature on the relation between different properties of the soil colloids, since it is only in the last few years that much work has been done on the isolated colloidal material. In a previous paper the authors pointed out the correspondence between variations in heats of wetting and in ammonia adsorption for a series of 13 colloids (*3*). Joseph, working with certain samples supplied by this bureau, noted a correspondence between tensile strength and adsorptive capacity (*27*). In the case of certain clay soils and fine soil fractions, which were doubtless largely colloidal, Hardy found a correspondence between the water held at maximum plasticity and the linear shrinkage of the material (*22*).

Since there is a fair degree of parallelism between variations in most of the laboratory properties of different soil colloids, it seems that a fairly good idea of the character of the colloidal material present in a given soil might be obtained by determining one or two properties. Possibly further investigation is needed before suggesting just what determinations should be selected for indicating the general character and behavior of a soil colloid. It appears, however, from the data already obtained, that the general behavior of a soil colloid might be predicted fairly well from a determination of the exchangeable bases and from a determination of either the heat of wetting or the adsorption of water vapor over moderately strong sulphuric acid. Also, the character of the colloid and its behavior would be fairly well indicated by its $\frac{SiO_2}{Al_2O_3+Fe_2O_3}$ ratio, as shown in the subsequent discussion.

Although these determinations would apparently characterize fairly well the general behavior of a colloid, they might not indicate the state of aggregation of a colloid in the soil. Possibly other determinations would prove more satisfactory for measuring changing conditions of a given colloid. In the case of several colloidal materials, viscosity determinations have been utilized for measuring changing states of aggregation in soils, but these may not be applicable to colloidal material as it exists in the soil.

RELATION BETWEEN PROPERTIES AND CHEMICAL COMPOSITION

The fact that different soil colloids tend to show corresponding variations in many of their properties was explained on the ground that these properties are probably dependent upon more fundamental properties of the colloids, such as the chemical nature, size,

and structure of the particles. Furthermore, the fact that a parallelism exists between properties which are presumably governed chiefly by structure and properties which are more strictly chemical was explained on the ground that structure and chemical nature of the soil colloids probably tend to vary together. The explanations given are rendered more probably by the fact that a correspondence obtains between many properties of the colloids and their chemical compositions. Some instances of such correspondence have been given in previous publications by Anderson and Mattson (*3*) and by Gile (*21*).

Other investigators have also noted a correspondence between certain properties of soil colloids or fine soil fractions and their chemical composition. Hardy (*22*) observed some relation between the $\frac{Al_2O_3+Fe_2O_3}{SiO_2}$ ratio, shrinkage, and the water content at maximum plasticity of certain clay fractions. Joseph and Hancock (*26*) pointed out that the $\frac{SiO_2}{Al_2O_3}$ ratio is connected with the extent the moisture-equivalent determination is modified by ignition of the material and by treatment with sodium carbonate. The correspondence however, is not marked. Later Joseph (*27*) called attention to a better correspondence between the $\frac{SiO_2}{Al_2O_3}$ ratio, imbitional water and rate of evaporation of several Sudan clays. Robinson and Holmes showed that there is some relationship between the ratio $\frac{SiO_2}{Al_2O_3+Fe_2O_3}$ and the color of soil colloids (*47, p. 25*).

The correspondence between variations in properties and in chemical composition of the colloids studied in this investigation is shown in Table 20. This table gives the molecular proportions of SiO_2 to Al_2O_3 plus Fe_2O_3 in the colloids, the exchangeable monovalent and divalent bases, and a summary of the properties expressed on the relative basis described on page 34.[23] The relative values for properties in this table are averages of the relative values given for individual properties in Table 19. The properties are grouped as described on page 35.

TABLE 20.—*Correspondence between properties and chemical composition of soil colloids*

Kind of colloid	$\frac{SiO_2}{Al_2O_3+Fe_2O_3}$	Exchangeable Ca+Mg+K+Na	Average relative values of properties in Group 1	Average relative values of properties in Group 2	Average relative values of all properties
Fallon	100	100	100	100	100
Sharkey	75	61	79	46	69
Marshall	56	44	48	45	51
Susquehanna	19	0	12	52	19
Sassafras	13	14	25	57	29
Huntington	4		12	6	15
Norfolk	0	0	13	8	9

[23] Several other chemical constituents and ratios of constituents show some correspondence with properties. This is to be expected, since, as previously pointed out (*47, p. 16*), certain constituents of the colloidal material tend to vary directly or indirectly with other constituents. Only the $\frac{SiO_2}{Al_2O_3+Fe_2O_3}$ ratio and the exchangeable bases are given in Table 20, however, since these, on the whole, correspond better with the properties.

It is apparent that variations in properties of the different colloids correspond fairly closely to variations in the exchangeable bases and to variations in the $\frac{SiO_2}{Al_2O_3+Fe_2O_3}$ ratio. The degree of correspondence between chemical composition and properties shown by these seven colloids is evidently not exceptional, inasmuch as many other colloids have been tested for single properties, and similar degree of correlation obtains between these single properties and chemical composition.

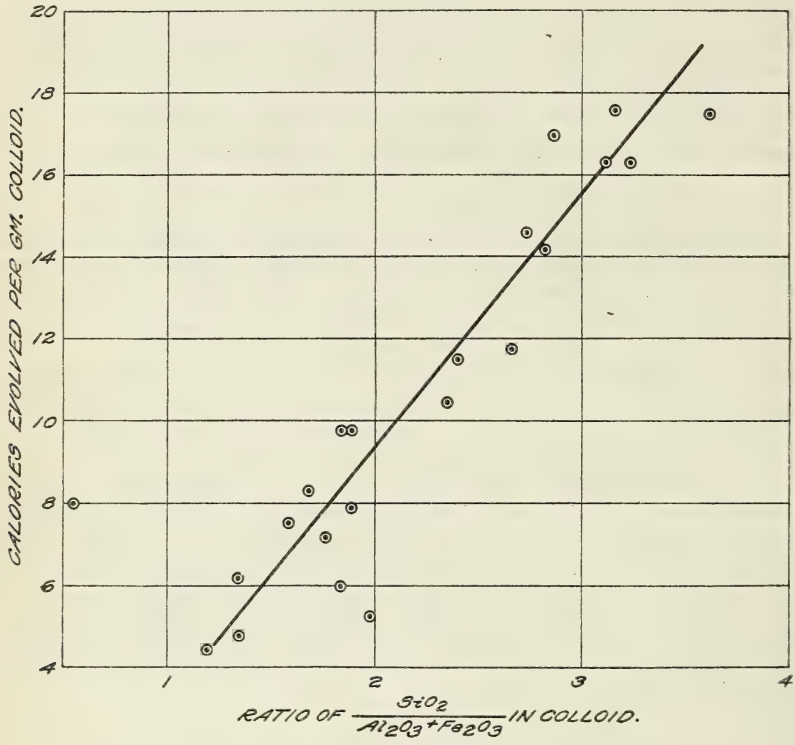

FIG. 2.—Relation between the heat of wetting and the $\frac{SiO_2}{Al_2O_3+Fe_2O_3}$ ratio of soil colloids

Figures 2, 3, and 4 show how the heat of wetting, ammonia adsorbed and malachite green adsorbed vary with the $\frac{SiO_2}{Al_2O_3+Fe_2O_3}$ ratio in the case of 22 to 32 different soil colloids. The data utilized in these curves were taken largely from previous publications (*2*, *20*, *47*).

These larger numbers of colloids show about the same order of correspondence between properties and silica ratio as the seven colloids in Table 20. A few colloids in each figure deviate considerably more than the others from the average relation between silica ratio and property. However, the colloids which deviate from the average relation in one property may conform to the average in another.

It is apparent from Table 20 that variations in the properties of the colloids correspond about as well to variations in the total content of exchangeable monovalent and divalent bases as to variations in the $\frac{SiO_2}{Al_2O_3+Fe_2O_3}$ ratio. Also, variations in the exchangeable bases follow the silica ratio fairly closely.

While the total exchangeable bases and silica ratio may be causally related, there is no indication of a causal relation between kind of exchangeable bases and silica ratio. There is no indication that

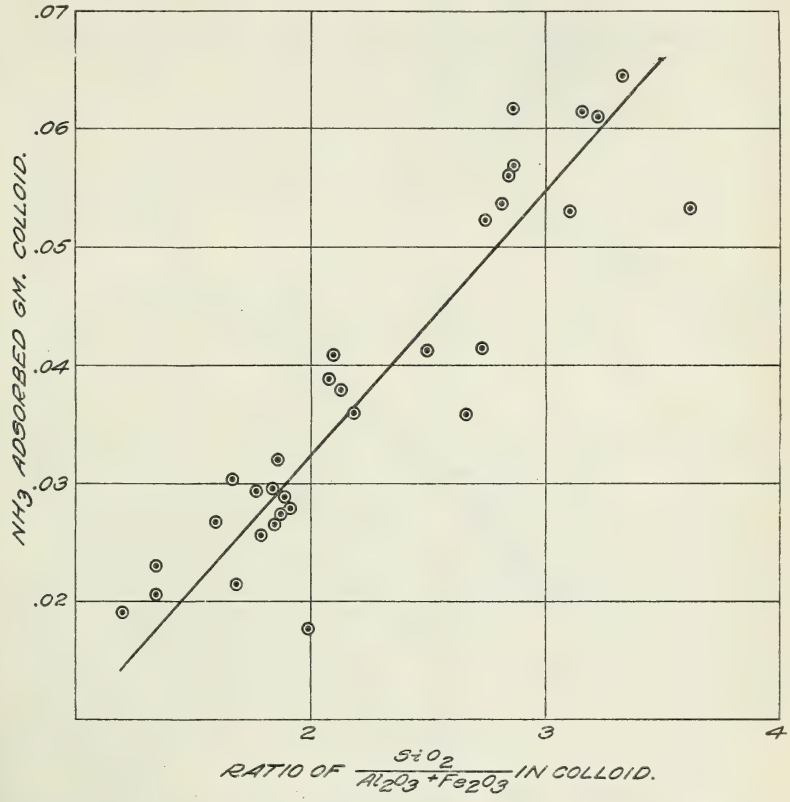

FIG. 3.—Relation between the NH_3 adsorbed by soil colloids and their $\frac{SiO_2}{Al_2O_3+Fe_2O_3}$ ratio

the silica ratio governs the kind of exchangeable bases. As a matter of fact, the proportions of exchangeable Ca, Mg, K, and Na given in Table 14 show little relation to the silica ratios, except that there is some correspondence between the proportion of Ca and Mg and the silica ratios.

The correspondence between $\frac{SiO_2}{Al_2O_3+Fe_2O_3}$ ratio and total content of exchangeable Ca, Mg, K, and Na might be explained on the ground that the natural conditions which have tended to bring about a certain silica ratio have tended to bring about also a certain content

of the exchangeable monovalent and divalent bases. Robinson and Holmes (*47*) have suggested that the $\frac{CaO + Na_2O}{Al_2O_3 + Fe_2O_3}$ ratio and the $\frac{SiO_2}{Al_2O_3 + Fe_2O_3}$ ratio may both be determined to a large extent by the rainfall to which the material has been subjected, the silica, like the lime, being more easily removed from the colloid than iron and alumina. It is also possible that the relative quantities of silica,

FIG. 4.—Relation between malachite green adsorption and the $\frac{SiO_2}{Al_2O_3 + Fe_2O_3}$

aluminium, and iron in the colloid determine to some extent the total content of exchangeable bases.

Some very general relations between silica ratio and kind of bases might be expected that are not brought out by the data given in this bulletin. For instance, a high proportion of exchangeable sodium would be expected only in colloids having a high silica ratio; since colloids high in exchangeable sodium are probably confined largely to the alkali or salt soils of arid regions, and it appears from the analyses reported by Robinson and Holmes (*47*) that the colloids of

arid soils are inclined to have high $\frac{SiO_2}{Al_2O_3+Fe_2O_3}$ ratios. However, a close correlation between high silica ratio and proportion of exchangeable sodium would not be expected, since sodium-saturated colloids do not appear to be the rule even in arid regions. On the other hand, exchangeable hydrogen or aluminum and iron should usually form a relatively high proportion of the exchangeable cations in colloids with low silicia ratios. It is generally recognized that exchangeable acidity is largely confined to weathered soils of the humid regions, and that the colloids of such soils tend to have low silica ratios. Evidently these general relations between the proportions of the different exchangeable bases and the proportions of silica to aluminum and iron in the colloid are not due to a direct influence of the silica ratio or the kind of exchangeable base, but are due to both these chemical characteristics being governed by similar or related soil-forming conditions.

The correlation between properties of the colloid and the silica ratio probably does not mean that all properties of the colloid are chiefly governed by the silica ratio directly. Structure of the colloid—that is, size and surface of the particles and arrangement or localization of the chemical constituents—must also influence properties of the soil colloidal material, just as structure influences the properties of other colloids. Furthermore, it should be borne in mind that the ratio of $\frac{SiO_2}{Al_2O_3+Fe_2O_3}$ takes into account only the chief constituents of the colloid and only the total quantity of these constituents. Other constituents of the colloid, such as organic matter, Ca, Mg, K, etc., would presumably have some effect on properties, and the condition of the elements in the colloid—that is, the form of combination in which they are present and their distribution in the colloid structure—should have an influence in determining properties. As a matter of fact, properties which are dependent upon the adsorption of cations, such as adsorption of malachite green and certain aspects of electrical behavior, are evidently governed more directly by the exchangeable Ca, Mg, etc., than by the silica ratio. However, as previously mentioned, the silica ratio may determine the exchangeable cations within certain limits.

It thus seems that the correlation between chemical constituents may be due in some cases to a direct and partial dependence of one constituent on another, and in other cases to both characteristics being dependent on similar or related conditions.

Further investigation is needed to learn in what measure properties are directly or indirectly dependent on the ratio of

$$\frac{SiO_2}{Al_2O_3+Fe_2O_3}.$$

It seems, however, that the connection between these major constituents of the colloid and properties may be indirect in many cases. Structure and the Ca, Mg, K, and Na present in an exchangeable condition may govern certain properties more directly than the silica ratio, but these may in turn be governed by the silica ratio to some extent.

CHARACTER OF SOIL COLLOIDS

Data are now available on the properties and ultimate chemical composition of a considerable number of different colloidal soil materials. It is thus possible to judge something of their general nature as compared with that of colloids which have been studied more extensively. All the extremes in composition and properties which might be encountered in colloidal soil materials probably are not represented in those studied in this and preceding publications, but the kinds of colloidal materials found in most soils are doubtless fairly well represented.

Although wide variations have been encountered in chemical composition and in all properties except specific gravity, the different soil colloids do not form sharply defined groups, since distinct gaps do not occur in chemical characteristics or properties when a sufficiently varied lot of colloids is examined. The colloids might, however, be divided roughly into "high," "medium," and "low" groups on the basis of chemical composition or on the basis of a number of properties. Rough grouping of soil colloids on many such bases coincide fairly well because of the correlations obtaining between different properties and between properties and chemical composition. Colloids, for instance, in the high group would usually have a high ratio of silica to aluminum and iron, a high content of total and exchangeable monovalent and divalent bases, and a relatively low content of water held at 110° C. (*47, p. 15*); the reaction in distilled water would be alkaline or only slightly acid and the average size of particles small; while comparatively high values would be shown for swelling, imbibition, moisture equivalent, volume of floc, heat of wetting, adsorptive capacity for vapors and electrolytes, and the quantity of methylene blue required to render the colloids isoelectric.

Soil colloidal materials as a class are evidently nearer the lyophobe than the lyophile type of colloid, judging by the degree they possess those properties which have been generally used for characterizing the two types. The soil colloids are much lower in viscosity, swelling, and imbibition, and are far less stable toward electrolytes than the typical lyophiles; but some of the colloids in the high group differ considerably from the typical lyophobes. The Fallon colloid, for instance, shows a volume increase in water of 150 per cent as compared with no increase for ignited silica gel and a 900 per cent increase for gelatin.

Bentonite appears to be closely related to the soil colloids, although its properties approach those of the lyophile colloids more nearly than most colloidal soil materials.

The characterization of the soil colloids as neither typically lyophile nor typically lyophobe accords with opinions of other investigators. Hardy (*22*) describes clay colloids as inelastic emulsoid gels with a reticulate structure. Bradfield (*9*) regards the finest colloidal soil material, that which is essentially submicroscopic, as an emulsoid, and the coarser material, made up of particles ranging from 0.4 to 1.2 microns in diameter, as a suspensoid.

This investigation has dealt only with the properties of the colloidal soil material and not with the properties of the whole soil. However, many of the properties of a soil are largely affected by

the colloidal material, some properties being governed by it almost exclusively (*1*, *2*), so that the results have an intimate bearing on the behavior of soils.

The results of this investigation emphasize the conclusion arrived at in previous studies—that, in order to explain satisfactorily the behavior of a soil, it is important to determine the kind as well as the quantity of colloidal material present. The fact that a soil contains 30 per cent or 50 per cent of colloid does not give much indication of the behavior of the soil unless the kind of colloidal material is specified. Some soils of warm humid regions with 70 per cent of colloidal material are more friable and permeable than soils containing 30 per cent of a colloidal material similar to the Fallon. It is true that the properties which have been studied are largely "laboratory" properties. But materials which differ so widely in their laboratory properties would obviously vary in their influence on such field properties of soils as permeability, response to applications of lime and fertilizer, tendency to erosion, cohesion, and the like.

SUMMARY

This investigation deals with the properties of colloidal materials isolated from widely different soils. Data are given on size of particles, specific gravity, adsorption of vapors, swelling, viscosity, volume of floc, adsorption of electrolytes, methylene blue required to render particles isoelectric, and hydrogen-ion concentration.

The different colloidal soil materials vary considerably in all properties except specific gravity.

A relationship between properties is indicated by the fact that variations of the colloids in one property usually parallel variations in other properties. The correlation between variations in the properties studied might be explained on the ground that these properties are dependent on a few more fundamental properties, such as chemical nature, size, and structure of particles, and that these more fundamental properties are related.

Variations in properties of the different colloids correspond fairly closely to variations in the exchangeable bases and to variations in the $\frac{SiO_2}{Al_2O_3+Fe_2O_3}$ ratio. The correlation between the properties and the silica ratio probably does not mean that all properties of the colloid are chiefly governed by the silica ratio directly. Certain properties are evidently governed more directly by the kind or quantity of exchangeable bases than by the silica ratio. However, the exchangeable bases and the silica ratio are usually correlated.

Soil colloids appear to be more lyophobe than lyophile in character, although they can not be looked upon as typical of either class.

The importance of determining kind as well as quantity of colloid in a soil is pointed out. It is suggested that one or two properties, or the $\frac{SiO_2}{Al_2O_3+Fe_2O_3}$ ratio, would characterize the kind of colloidal material fairly well.

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